Intramolecular Diels–Alder Reaction with Furans: Effect of the Substitution Pattern Reinvestigated

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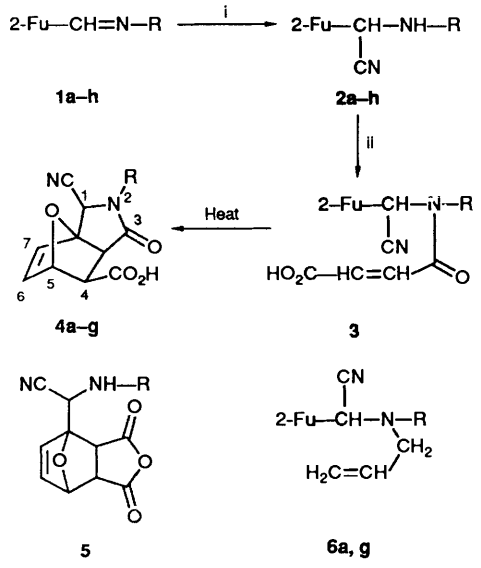
Intramolecular Diels–Alder reactions occurred smoothly when *N*-(α-cyanofurfuryl)arylamines **2a–g** and *N*-furfurylarylamines **7a–d** were treated with maleic anhydride and fumaroyl chloride–triethylamine respectively, to afford the corresponding cycloadducts **4** and **10** in good yields. Electron-withdrawing groups and the cyano group inhibited the IMDA reaction when a less activated dienophile was employed. The structures of these IMDA products were fully characterised on the basis of spectral results and elemental analyses.

Both intermolecular and intramolecular Diels–Alder (IMDA) reactions of furans[1] are of continuing interest, many heterocycles[2] and natural products having been synthesised from them.[3] This approach is attractive since oxygen is readily extruded from the cycloadduct and a variety of suitably functionalised furans is readily available. Inherent limitations on the method are posed by the substitution pattern[4] associated with both the connecting chain and the bridging chain, even simple ethers[5] and esters[2a] having been reported to inhibit the Diels–Alder reaction as a result of conformational effects. Further, the use of high pressure[6] and temperature are also reported to be counterproductive because of the reversible nature of these reactions. Interestingly, Diels–Alder reactions of simpler compounds, *e.g.* furfuryl alcohol and furfurylamines, have been the subject of controversy[7] much effort being devoted to understanding the factors which influence the inter/intramolecular pathways adopted. We now report work employing *N*-furfurylarylamines[8] as the dienes.

Results and Discussion

The *N*-(α-cyanofurfuryl)arylamines **2** were easily available in good yield in two steps from the corresponding *N*-furfurylideneaniline[9] following its cyanation. A recurring problem encountered in this sequence (formation of violet coloured resin *i.e.* the Stenhouse dye)[10] was circumvented using carefully controlled *in situ* hydrocyanation of imines. Cyanation *via* trimethylsilyl cyanide also gave cyano amines in comparable yields to the hydrocyanic addition method, although in neither case were the dye or other ring-transformed compounds observed. The cyano amine **2a** when treated with an equimolar amount of maleic anhydride in refluxing benzene for 1 h gave **4a** (75%) as a semisolid. The structural assignment of **4a** was based on spectral evidence and its elemental analysis (see Experimental section) and confirmed that it arose by an IMDA reaction. The absence of anhydride and NH absorption in the IR region ruled out the possibility of structure **5**[11] resulting from an intermolecular Diels–Alder reaction. In its ^{1}H NMR spectrum the proton chemical shifts and the coupling constants were confirmed by decoupling protons 1-H, 2-H, 3-H, 5-H and 6-H: a coupling constant of 9 Hz for 5-H with 6-H clearly indicating a *cis* geometrical relationship between them. Similarly, treatment of the cyano amine **2h** with maleic anhydride gave solely the acyclic product **3h**, there being no evidence for the formation of any IMDA product. Forcing conditions (temperature, pressure and phase-transfer catalysis) were ineffective in cyclising compound **3h**.*

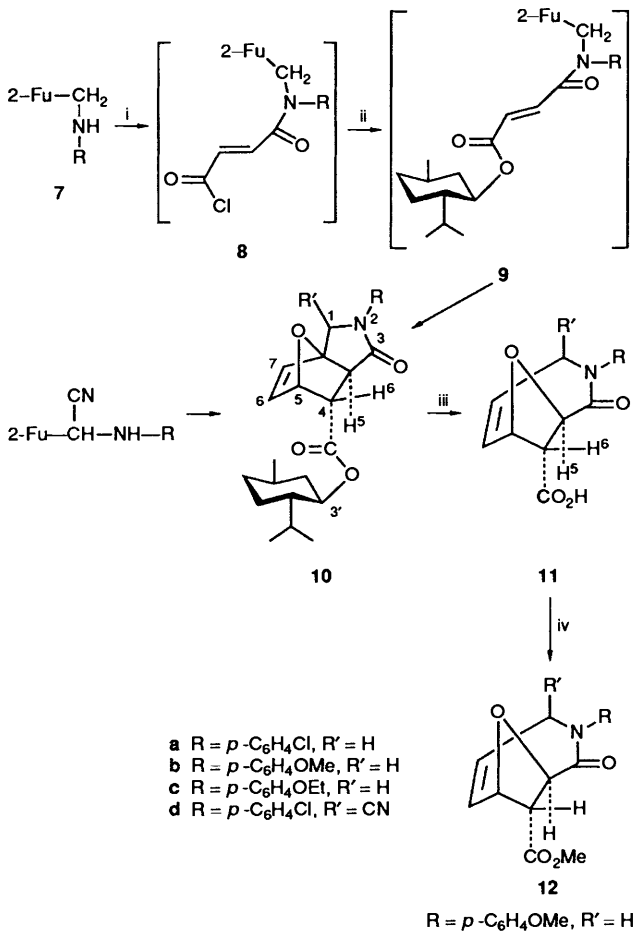


Scheme 1 *Reagents:* i, AcOH–NaCN–water; ii, maleic anhydride in benzene (dry)

Preparation of the IMDA product **10** by *in situ* generation of the imido esters **9** involves three steps (*i.e.* imide formation, esterification and subsequent intramolecular Diels–Alder reaction) carried out in a one-pot reaction (see Scheme 2). The imide, prepared from *N*-furfuryl-*p*-chloroaniline **7a** and fumaroyl chloride in the presence of triethylamine, was esterified with optically pure menthol **9a**; this underwent spontaneous intramolecular cyclisation with the furan, to yield the IMDA adduct **10a** (65%) > 98% d.e.; $[\alpha]_D^{18}$ −35.58 (*c* 4.0, $CHCl_3$). The structure of **10a** was established on the basis of spectral results and elemental analyses. A coupling constant 3 Hz for 5-H and 6-H in the δ_H NMR spectrum clearly indicate their *trans* relationship. Similarly, IMDA products **10b–d** were prepared and the physical constants and spectroscopic data are recorded in the Experimental section. Saponification of **10b** with sodium methoxide removed the chiral group to give the epoxyisoindoline **11** (70%). The IMDA product **11** R = (*p*-C_6H_4OMe) was then treated with diazomethane to afford the esterified product **12** (75%) with an e.e. of 90%.

We have studied the use of allyl bromide in IMDA reactions using *N*-furfurylarylamines, reported to be very slow and reversible,[12] and have found that in a two-phase system (PTC)

* Results for compound **3h**: m.p. 142–143 °C (66%); δ_H(60 MHz, $CDCl_3$) 1.40 (3 H, d, CH_3), 4.02–4.35 (2 H, m) and 6.00–7.60 (10 H, m); ν_{max}/cm^{-1} (KBr) 1650 and 2120; *m/z* 324 (M^+) (Found: C, 66.8; H, 4.8; N, 8.5. $C_{18}H_{16}N_2O_4$ requires C, 66.66; H, 4.93; N, 8.64%).



Scheme 2 *Reagents*: i, Fumaroyl chloride, TEA; ii, menthol, TEA; iii, NaOMe, MeOH; iv, CH_2N_2, Et_2O

the cycloadducts are quickly formed in higher than reported yields.[8,13] In view of this, we were encouraged to treat **2a** with allyl bromide both under normal thermolytic conditions and employing PTC as described earlier. This produced not the expected IMDA product but rather the *N*-allylated product **6a** (25%); this failed to cyclise under forcing conditions (pressure at 100 °C for 2.5 h). The presence of furan as well as olefinic protons in the ^1H NMR spectrum of **6a** clearly ruled out the formation of an IMDA product. This study suggests that either the cyano group has inhibited the cyclisation because of its bulk or because of its electron-withdrawing nature; in either case cycloadduct formation is precluded.

Experimental

M.p.s were determined using a Buchi melting point apparatus and are uncorrected. The IR spectra were recorded in KBr discs on a Perkin-Elmer 237B IR spectrophotometer. Microanalyses were performed on a Perkin-Elmer 240C analyser. The ^1H NMR spectra were recorded on a 90 MHz spectrometer and chemical shift values are recorded in units relative to Me_4Si as internal standard; *J* values are given in Hz. The imines **1** were prepared by mixing freshly distilled furfuraldehyde and the appropriate amine in methanol at 0–5 °C. The reaction was complete in 5–10 min and the solid imines were obtained on dilution with ice-cold water followed by crystallisation from suitable solvents. Light petroleum had b.p. 60–80 °C and ether was diethyl ether. The optical rotations were recorded on optical activity model AA1000 polarimeters; $[\alpha_D]$ values are recorded in 10^{-1} deg cm^2 g^{-1}. Liquid chromatographic experiments were performed on tribenzoylcellulose.

Preparation of α-Cyanofurfurylamine **2a–h**.—Aqueous sodium cyanide (98 mg, 2 mmol) was added dropwise over 5–10 min to a stirred solution of *N*-furfurylidene-*p*-anisidine **1a** (402 mg, 2 mmol) in methanol (70 cm^3) and glacial acetic acid (120 mg, 2 mmol). The exothermic reaction was cooled in ice-cold water. After 30 min the precipitated nitrile was filtered off, washed with water to remove cyanide ion (silver nitrate test) and recrystallised from methanol to give the product (80%), m.p. 94–95 °C. Similarly, other nitriles **2b–h** were prepared.

Preparation of Epoxyhexahydroisoindole Derivatives **4a–g**.—A mixture of α-cyanofurfurylamine **2a** (456 mg, 2 mmol), dry benzene (30 cm^3) and maleic anhydride (196 mg, 2 mmol) in a flask equipped with a reflux condenser was stirred at room temperature for 10 min and then heated in an oil-bath. The temperature of the mixture was allowed to increase slowly just to reflux at which temperature it was maintained for 1 h. Benzene was then distilled off on a rotary evaporator and the residue **4a** was treated with benzene–light petroleum (1 : 4). The absence of temperature control reduced the yields to 30–40%. Similarly, compounds **4b–g** were prepared.

4a M.p. 168–170 °C (75%); ν_{max}/cm^{-1} (KBr) 1630, 1700 and 2130; *m/z* 326 (M^+) (Found: C, 62.4; H, 4.3; N, 8.4. $C_{17}H_{14}N_2O_5$ requires C, 62.57; H, 4.29; N, 8.58%); δ_H(400 MHz, $CDCl_3$) 2.92 (1 H, d, *J* 9, 3a-H), 3.21 (1 H, d, *J* 9, 4-H), 3.61 (3 H, s, OMe), 5.06 (1 H, s, 1-H), 5.40 (1 H, d, *J* 2, 5-H), 6.62 (1 H, dd, *J* 6, 2, 6-H), 6.82 (1 H, d, *J* 6, 7-H), 6.95–7.42 (4 H, m, ArH) and 11.45 (1 H, s, COOH).

4b M.p. 189–191 °C (70%); δ_H(90 MHz, $CDCl_3$) 2.25 (3 H, s, Me), 2.90 (1 H, d, 3a-H), 3.20 (1 H, d, 4-H), 4.90 (1 H, s, 1-H), 5.10 (1 H, d, 5-H), 6.20–7.20 (6 H, m, 6-H, 7-H, ArH) and 11.45 (1 H, s, COOH); ν_{max}(KBr)/cm^{-1} 1640, 1705, 1720, 2125 and 2900; *m/z* 310 (M^+) (Found: C, 65.75; H, 4.4; N, 9.2. $C_{17}H_{14}N_2O_4$ requires C, 65.81; H, 4.51; N, 9.03%).

4c M.p. 184–185 °C (72%); δ_H(90 MHz, $CDCl_3$) 2.80 (1 H, m, 3a-H), 3.21 (1 H, m, 4-H), 4.85 (1 H, s, 1-H), 5.10 (1 H, d, 5-H), 6.25–7.30 (6 H, m, 6-H, 2-H, ArH) and 11.50 (1 H, s, CO_2H); ν_{max}/cm^{-1} (KBr) 1635, 1695, 1710, 2120 and 2675; *m/z* 376 (M^+) (Found: C, 51.1; H, 3.05; N, 7.6. $C_{16}H_{11}N_2O_4Br$ requires C, 51.20; H, 2.93; N, 7.47%).

4d M.p. 176–177 °C (75%); δ_H(90 MHz, $CDCl_3$) 2.85 (1 H, m, 3a-H), 3.15 (1 H, m, 4-H), 4.90 (1 H, s, 1-H), 5.15 (1 H, d, 5-H), 6.25–7.20 (6 H, m, 6-H, 7-H, ArH) and 11.42 (1 H, s, CO_2H); ν_{max}(KBr)/cm^{-1} 1630, 1700, 1715, 2125 and 2700; *m/z* 330 (M^+) (Found: C, 58.25; H, 3.4; N, 8.6. $C_{16}H_{11}ClN_2O_4$ requires C, 58.18; H, 3.33; N, 8.48%).

4e M.p. 170–172 °C (68%); δ_H(90 MHz, $CDCl_3$) 1.20 (3 H, t, Et), 2.90 (1 H, m, 3a-H), 3.15 (1 H, m, 4-H), 3.90 (2 H, q, OCH_2), 4.85 (1 H, s, 1-H), 5.10 (1 H, d, 5-H), 6.48–7.42 (6 H, m, 6-H, 7-H, ArH), 11.40 (1 H, s, CO_2H); ν_{max}(KBr)/cm^{-1} 1630, 1705, 1715, 2130 and 2750; *m/z* 340 (M^+) (Found: C, 63.6; H, 4.6; N, 8.1. $C_{18}H_{16}N_2O_5$ requires C, 63.53; H, 4.70; N, 8.23%).

4f M.p. 187–188 °C (71%); δ_H(90 MHz, $CDCl_3$) 2.85 (1 H, m, 3a-H), 3.20 (1 H, m, 4-H), 4.84–5.25 (4 H, m, 5-H, 1-H, CH_2), 6.15–7.00 (7 H, m, 6-H, 7-H, ArH) and 11.45 (1 H, s, CO_2H); ν_{max}(KBr)/cm^{-1} 1700, 1720, 2130 and 2850; *m/z* 310 (M^+) (Found: C, 66.0; H, 4.6; N, 9.2. $C_{17}H_{14}N_2O_4$ requires C, 65.80; H, 9.51; N, 9.03%).

4g M.p. 152–153 °C (65%); δ_H(90 MHz, $CDCl_3$) 2.85–3.20 (5 H, m, 3a-H, 4-H, Me), 4.95 (1 H, s, 1-H), 5.30 (1 H, d, 5-H), 6.50–6.85 (2 H, m, 6-H, 7-H) and 11.35 (1 H, s, CO_2H); ν_{max}(KBr)/cm^{-1} 1640, 1700, 1720, 2130 and 2800; *m/z* 234 (M^+) (Found: C, 56.6; H, 4.4; N, 11.8. $C_{11}H_{10}N_2O_4$ requires C, 56.41; H, 4.27; N, 11.96%).

Reaction of N-*Furfurylarylamines and* α-*Cyanofurfuryl-amines with Fumaroyl Chloride.*—Fumaroyl chloride (0.152 g, 1 mmol) was added slowly to a solution of *N*-furfuryl-*p*-chloroanaline **7a**, (0.207 g, 1 mmol) dissolved in chloroform (10 cm^3) and cooled in an ice–salt bath. Dry triethylamine (0.151 g, 1.5 mmol) diluted with anhydrous chloroform (5 cm^3) was then added very slowly by means of a dropping funnel to the reaction mixture, the temperature being maintained strictly < -5 °C. After complete addition the temperature was allowed to rise to 5 °C when a TLC check showed complete consumption of **7a**; the temperature of the reaction mixture was then lowered to -10 °C. After this (−)-menthol (0.156 g, 1 mmol) was added to the reaction mixture followed by dropwise addition of dry triethylamine (0.101 g, 1 mmol) diluted with absolute chloroform (5 cm^3); the temperature of the reaction mixture was then slowly raised to the boiling point. After 20 min under reflux the magnetically stirred mixture showed by TLC that the reaction was complete: solvent was removed under reduced pressure and the resulting solid was purified by column chromatography using light petroleum–ethyl acetate (9:1) as eluent. The IMDA product **10a** thus obtained was recrystallised from benzene–light petroleum (1:4), and had m.p. 133–134 °C (65%); ν_{max}(KBr)/cm^{-1} 1690 and 1750; *m/z* 443 (M^+) (Found: C, 67.5; H, 6.85; N, 3.3. $C_{25}H_{30}ClNO_4$ requires C, 67.7; H, 6.8; N, 3.2); δ_H 0.70–2.10 (18 H, m all from menthyl group), 3.15 (1 H, d, *J* 3, 3a-H), 3.57 (1 H, dd, *J* 5, 3, 4-H), 4.10 (1 H, d, *J* 11, 1-H), 4.45 (1 H, d, *J* 11, 1-H), 4.63 (1 H, m, 3′-H), 5.30 (1 H, dd, *J* 5, 2 Hz), 5-H), 6.30 (1 H, dd, *J* 6, 2, 6-H), 6.64 (1 H, d, *J* 6, 7-H) and 7.30–7.60 (4 H, m, ArH). Similarly compounds **10b–d** were prepared.

10b M.p. 128–129 °C (68%); >98% d.e.; $[\alpha]_D^{18}$ −36.90 (*c* 4.0, $CHCl_3$) all from methyl group; δ_H(100 MHz, $CDCl_3$) 0.70–2.10 (18 H, m), 3.15 (1 H, d), 3.57 (1 H, dd), 3.81 (3 H, s), 4.10 (1 H, d), 4.45 (1 H, d), 4.65 (1 H, m), 5.30 (1 H, dd), 6.30 (1 H, dd), 6.65 (1 H, d) and 7.25–7.60 (4 H, m); ν_{max}(KBr)/cm^{-1} 1695 and 1745; *m/z* 439 (M^+) (Found: C, 71.2; H, 7.6; N, 3.2. $C_{26}H_{33}NO_5$ requires C, 71.07; H, 7.51; N, 3.19%).

10c M.p. 135–136 °C (62%) >98% d.e.; $[\alpha]_D^{18}$ −38.53 (*c* 4.0, $CHCl_3$) δ_H(100 MHz, $CDCl_3$) 0.70–2.10 (21 H, m), 3.10 (1 H, d), 3.57 (1 H, dd), 3.90 (2 H, q), 4.15 (1 H, d), 4.48 (1 H, d), 4.65 (1 H, m), 5.30 (1 H, dd), 6.30 (1 H, dd), 6.64 (1 H, d), 7.30–7.62 (4 H, m). ν_{max}(KBr)/cm^{-1} 1700 and 1750; *m/z* 453 (M^+) (Found: C, 72.5; H, 7.85; N, 3.25. $C_{27}H_{35}NO_5$ requires C, 72.62; H, 7.72; N, 3.17%).

10d M.p. 163–164 °C (65%); 50% d.e.; $[a]_D^{18}$ −29.13 (*c* 4.0, $CHCl_3$); δ_H(100 MHz, $CDCl_3$) 0.65–2.05 (18 H, m), 3.35 (1 H, m), 3.60 (1 H, m) 4.65 (1 H, m), 5.00 (1 H, s), 5.40 (1 H, dd), 6.45 (1 H, m), 6.85 (1 H, m) and 7.35–7.60 (4 H, M); ν_{max}-(KBr)/cm^{-1} 1695, 1700 and 2140. *m/z* 468 (M^+) (Found: C, 66.8; H, 6.1; N, 6.1. $C_{26}H_{29}N_2O_4$ requires C, 66.6; H, 6.19; N, 5.98%).

Saponification of **10b** was effected by stirring equimolar quantities of **10b** (2.19 g, 5 mmol) and sodium methoxide (0.270 g, 5 mmol) in methanol (20 cm^3) at 60 °C for 4 h. The solvent was then distilled off and the residue was chromatographed using chloroform as the eluent to give the epoxyisoindoline **11** (70%), m.p. 180–182 °C; ν_{max}(KBr)/cm^{-1} 1665, 1730, 1755 and 2955; *m/z* 301 (M^+) (Found: C, 63.9; H, 5.1; N, 4.5. $C_{16}H_{15}NO_5$ requires C, 63.78; H, 4.98; N, 4.65%); δ_H 2.95 (1 H, d, 3a-H), 3.07 (1 H, d, 4-H), 3.20 (3 H, s, OMe), 4.23 (1 H, d, one of 1-H), 4.58 (1 H, d, other 1-H), 5.30 (1 H, dd, 5-H), 6.25 (1 H, dd, 6-H), 6.47 (1 H, d, 7-H), 7.05–7.55 (4 H, m, ArH) and 11.45 (1 H, s, COOH).

Esterification of **11** *with Diazomethane.*—To a magnetically stirred suspension of the epoxyhexahydroisoindoline derivative **11** (301 mg, 1 mmol) in ether (20 cm^3) cooled in an ice-bath was added in small portions an ethereal solution of diazomethane. After 10 h (monitored by TLC), the ether was removed and the residue was purified by column chromatography using chloroform–ethyl acetate (1:1) as eluent to give the esterified product **12** (75%) with an e.e. >90%; $[\alpha]_D^{20}$ −15.76 (*c* 1.3, $CHCl_3$), M.p. 143–144 °C, δ_H 2.92 (1 H, d, 3a-H), 3.10 (1 H, d, 4-H), 3.16 (3 H, s, CO_2Me), 3.30 (3 H, s, OMe), 4.23 (1 H, d, one of 1-H), 4.60 (1 H, d, other 1-H), 5.32 (1 H, dd, 5-H), 6.25 (1 H, dd, 6-H), 6.45 (1 H, d, 7-H) and 7.05–7.65 (4 H, m, ArH); *m/z* 315 (M^+) (Found: C, 64.9; H, 5.6; N, 4.35. $C_{17}H_{17}NO_5$ requires C, 64.76; H, 5.49; N, 4.44%).

Reaction of N-(α-*Cyanofurfuryl*)*amine* **2a** *with Allyl Bromide.*—*Under thermolytic conditions.* Freshly distilled allyl bromide (484 mg, 4 mmol) was added at room temperature to a stirred suspension of the amine **2a** (456 mg, 2 mmol), anhydrous sodium carbonate (212 mg, 2 mmol) and tetrabutylammonium bromide (10 mg) in dry benzene and the mixture was heated under reflux in an oil-bath. After 3 h, benzene was distilled off under reduced pressure and the residue was purified by silica gel column chromatography using light petroleum-ethyl acetate (8:2) as the eluent to give the acyclic product **6a** (10%).

Under pressure. A mixture of the amine **2a**, (228 mg, 1 mmol), dry benzene (10 cm^3), anhydrous sodium carbonate (106 mg, 1 mmol) and allyl bromide (242 mg, 2 mmol) in a sealed tube was heated in an autoclave at 100 °C for 2–3 h. The solution was decanted from resinous material and further purified by column chromatography using light petroleum–ethyl acetate (9:1) as the eluent to give the acyclic product **6a** (25%); δ_H(60 MHz, $CDCl_3$) 3.25 (3 H, s, OMe), 3.35 (2 H, d), 4.45–5.65 (4 H, m) and 6.35–7.15 (4 H, m); ν_{max}(KBr)/cm^{-1} 2210 (Found: C, 71.5; H, 6.1; N, 10.6. $C_{16}H_{16}N_2O_2$ requires C, 71.64; H, 5.97; N, 10.44%). Similarly, when the amine **2g** was treated with allyl bromide in the presence of sodium carbonate under pressure (sealed tube), the acyclic adduct **6g** was obtained exclusively as oily material (20%), there being no evidence for IMDA product formation; δ_H(60 MHz, $CDCl_3$) 2.40 (3 H, s, Me), 4.15–5.40 (6 H, m), 6.20 (2 H, m, furan) and 7.20 (7 H, d, furan); ν_{max}(KBr)/cm^{-1} 2120 (Found: C, 68.0; H, 7.0; N, 15.8. $C_{10}H_{12}N_2O$ requires C, 68.18; H, 6.82; N, 15.91%).

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