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A new method of constructing dearomatized compounds using triazene

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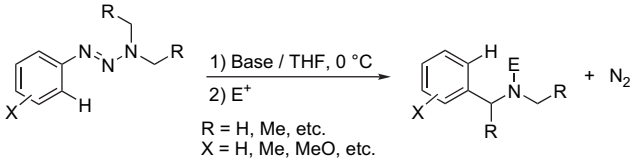
Abstract—We are reporting on a new method of constructing dearomatized compounds from α-substituted aryltriazenes. Deprotonation occurs at C atom α to N3. Nucleophilic attack of generated anion at the *ortho*-position of aryl group forms a new carbon–carbon bond. A stereoselective reaction was observed when the substituents on the C α to N3 are tied together in either a pyrrolidine or a piperidine. The product of this reaction possessed an interesting dearomatized tetrahydrobenzotriazine framework.

1. Introduction

Destroying the aromaticity of a benzene ring is a powerful strategy for the synthesis of cyclohexane derivatives. The Birch reduction,[1] Reimer–Tiemann,[2] and Alder reactions[3] are well-known methods of constructing dearomatized compounds. Recently some new methods have been reported: oxidation with *Pseudomonas putida*;[4] electrophilic addition of an osmium–arene complex;[5] nucleophilic addition to a chromium–arene complex;[6] an aluminum tris(2,6-diphenylphenoxide) (ATPH)-promoted nucleophilic addition to aromatic aldehydes and ketones;[7] radical cyclization;[8] the thia-Sommelet reaction;[9] anion cyclization of *N*-benzylbenzamides;[10] and phosphoramides.[11] 3,3-Dialkyl-1-aryltriazenes are also used in many ways in organic syntheses.[12] We previously reported on the transformation of aryltriazene compounds to benzylamine derivatives including an intramolecular C–C bond formation with N_2 releasing and discussed the preliminary results of the dearomatization reaction of aryltriazenes (Scheme 1).[13]

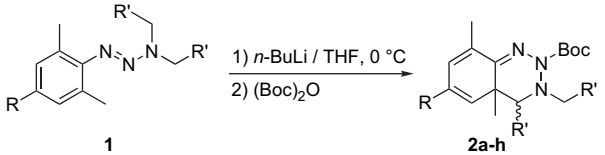


Scheme 1. Formation of benzylamine.

We obtained additional significant results through further investigation into the course of these reactions. When we treated 3,3-dialkyl-1-aryltriazenes possessing substituents at both the second and sixth positions on the aryl group with *n*-BuLi, we obtained new dearomatized heterocyclic compounds in good to moderate yields.

2. Results and discussion

The results are summarized in Scheme 2 and Table 1. In the case of R′=Me, we obtained two diastereomers (entries 2 and 6). In each case the minor product was unstable and decomposed slowly. On the other hand, triazenes derived from pyrrolidine (entries 3 and 7) and piperidine (entries 4 and 8) provided a single diastereomer in both cases.



Scheme 2. Formation of dearomatized compounds.

We determined the molecular structures of the products (**2a**–**h**) by their spectral data. The aromatic protons and carbons were disappeared and the newly appeared olefin protons and carbons were observed by NMR spectra. Fortunately the single crystal of **2d** was obtained, and the structure was confirmed by X-ray crystallography (Fig. 1).[14] The planar-like three rings system was constructed and the relative

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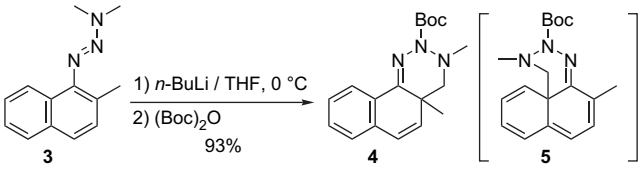
Table 1. Results of dearomatization reactions

Entry	Triazene **1**		Product	Yield (%)
	R	R′		
1	H	H	**2a**	73
2	H	Me	**2b**	64 (1:2.9)
3	H	$-(CH_2)_2-$	**2c**	75
4	H	$-(CH_2)_3-$	**2d**	58
5	Me	H	**2e**	65
6	Me	Me	**2f**	52 (1:5)
7	Me	$-(CH_2)_2-$	**2g**	85
8	Me	$-(CH_2)_3-$	**2h**	63

configuration of the substituents on C2 and C9 was *syn*. The bond length of N1–N2 was 1.391 Å and that of N2–N3 was 1.453 Å. It is known that the N–N bond length of hydrazine is 1.453 Å. The newly generated bond of C2–C9 was 1.554 Å.

In the case of 3,3-dimethyl-1-(2-methylnaphthyl)triazene (**3**), the C–C bond formation occurred selectively at the second position to form **4** in 93% yield, and we did not observe **5** (Scheme 3). Since one aromatic ring remained in product **4**, we presumed that **4** was more stable than **5**.

No dearomatized heterocyclic compounds of these types have ever been reported. The dearomatized heterocyclic



Scheme 3. Regioselectivity of reaction of **3** with base.

compounds possess interesting structures, specifically one quaternary or vicinal quaternary and tertiary carbons conjugated with a hydrazone group. Therefore, these compounds may play a part as valuable synthons in organic syntheses.

As mentioned above, we observed stereoselectivities in the newly formed vicinal quaternary and tertiary carbons. To investigate this stereoselectivity in the formation of **2d**, we examined the course of the reaction of **6** by semiempirical molecular orbital calculations (PM3 method) (Scheme 4).[15] The heat of the formation energy of the *anti* isomer **10** was 0.8 kcal/mol lower than that of *syn* isomer **8**, which was the precursor of **2d**. In transition states, however, the energy of **7** was lower than that of **9** by 1.3 kcal/mol. This evidence suggests that the reaction proceeded under kinetic control.

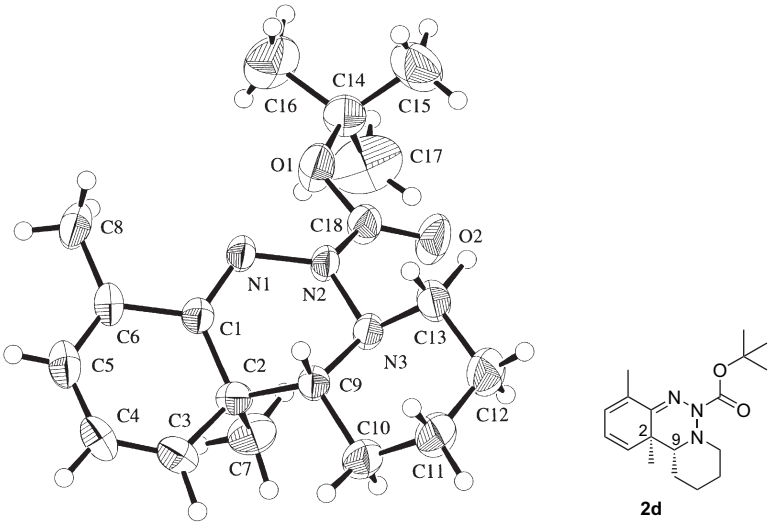
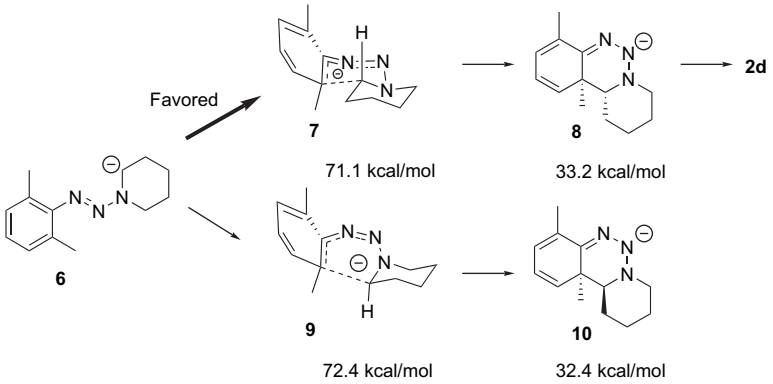


Figure 1. Perspective view of compound **2d**.



Scheme 4. Theoretical analysis of stereoselectivity of **2d**.

3. Conclusion

We have revealed new dearomatized reactions including an intramolecular C–C bond formation from 3,3-dialkyl-1-aryltriazenyl compounds. This reaction provides a new synthetic route for six-membered ring compounds from benzene derivatives. These products possess an interesting structure, one quaternary or vicinal quaternary and tertiary carbons conjugated with a hydrazone group. In addition, the configuration of the substituents of the newly formed C–C bond formation was exclusively *syn* when the anion formed triazene was bound as part of either a pyrrolidine or a piperidine. This stereoselectivity depended on the energy difference of the intermediate in the carbon–carbon bond forming stage. Since these new dearomatized compounds have a brand-new and interesting framework, we expect that these compounds will play the important role in the synthesis of drugs and functional compounds as new potential synthons.

4. Experimental

4.1. General methods

NMR spectra were recorded on JEOL GSX-270 (^{1}H 270 MHz, ^{13}C 67.5 MHz) spectrometer in $CDCl_3$ or CD_3OD with TMS as an internal standard. Mass spectra (EI) were recorded on a JMS-HX100 spectrometer. Infrared spectra were recorded on a Shimadzu IR-435 spectrophotometer. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was freshly distilled under nitrogen from sodium benzophenone ketyl prior to use.

4.2. General procedure for the transformation of triazenes into tetrahydrobenzotriazine derivatives

To a solution (0.5–1 M) of triazene (**1**) in dry THF (2 mL) was added dropwise a solution of *n*-BuLi/hexane (1 equiv) at 0 °C. After stirring for 1 h, the reaction mixture was quenched with Boc_2O (1.5 equiv). Extractive work-up and the subsequent purification afforded tetrahydrobenzotriazine derivatives (**2**).

4.2.1. *tert*-Butyl 3,4a,8-trimethyl-4,4a-dihydrobenzo[*d*][1,2,3]triazine-2(3*H*)-carboxylate (2a). Oil, 73%; ^{1}H NMR ($CDCl_3$) δ: 6.15 (dsep, J=6.0, 2.0 Hz, 1H), 5.93 (dd, J=9.0, 6.0 Hz, 1H), 5.79 (dt, J=9.0, 0.7 Hz, 1H), 3.60 (d, J=13.0 Hz, 2H), 3.28 (d, J=13.0 Hz, 2H), 2.51 (s, 3H), 2.08 (t, J=0.7 Hz, 3H), 1.56 (s, 9H), 1.17 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 160.96, 152.45, 137.78, 131.17, 125.95, 121.20, 81.67, 63.97, 40.11, 33.68, 28.23, 26.94, 16.54; IR (neat) cm^{-1}: 2950 (m), 1720 (s), 1560 (w), 1450 (m), 1400 (m), 1360 (m), 1320 (s), 1250 (m), 1140 (s), 870 (w), 720 (m); MS (EI) (*m*/*z*, %): 277 (M$^+$, 2.5), 177 (16), 162 (28), 133 (13), 119 (21), 105 (58), 91 (10), 77 (10), 57 (100), 41 (19); HRMS: 277.1805 (Calcd for $C_{15}H_{23}N_3O_2$, 277.1790).

4.2.2. *tert*-Butyl 3-ethyl-4,4a,8-trimethyl-4,4a-dihydrobenzo[*d*][1,2,3]triazine-2(3*H*)-carboxylate (2b). Brown oil, 48% as a major product; ^{1}H NMR ($CDCl_3$) δ: 6.26 (dt, J=6.0, 1.5 Hz, 1H), 5.97 (dd, J=9.0, 2.0 Hz, 1H), 5.87 (d, J=9.0 Hz, 1H), 3.17 (q, J=7.0 Hz, 1H), 2.54 (m, 2H), 2.10 (s, 3H), 1.53 (s, 9H), 1.29 (d, J=7.0 Hz, 3H), 0.97 (t, J=7.0 Hz, 3H), 0.96 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 167.52, 153.59, 138.32, 130.91, 127.57, 119.68, 80.57, 66.78, 48.20, 38.74, 28.20, 20.00, 16.69, 16.01, 11.93; IR (neat) cm^{-1}: 2950 (m), 1700 (s), 1540 (w), 1450 (m), 1400 (s), 1330 (s), 1250 (m), 1140 (s), 900 (m), 720 (s); MS (EI) (*m*/*z*, %): 305 (M$^+$, 15), 204 (9), 105 (100), 72 (36), 57 (66); HRMS: 305.2122 (Calcd for $C_{17}H_{27}N_3O_2$, 305.2103).

4.2.3. *tert*-Butyl 7,10a-dimethyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]triazine-5(10a*H*)-carboxylate (2c). Brown oil, 75%; ^{1}H NMR ($CDCl_3$) δ: 5.97 (dt, J=6.0, 1.5 Hz, 1H), 5.93 (dd, J=9.0, 6.0 Hz, 1H), 5.74 (d, J=9.0 Hz, 1H), 3.87 (dt, J=9.0, 4.0 Hz, 1H), 3.26 (dd, J=7.5, 2.5 Hz, 1H), 3.10 (dt, J=9.0, 7.5 Hz, 1H), 2.18 (m, 2H), 2.05 (s, 3H), 1.85 (m, 2H), 1.57 (s, 9H), 1.11 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 152.15, 149.94, 132.33, 131.93, 123.61, 121.89, 81.97, 55.10, 53.63, 37.48, 28.16, 23.31, 19.75, 16.79; IR (neat) cm^{-1}: 2900 (m), 1720 (s), 1540 (w), 1450 (m), 1400 (m), 1360 (s), 1310 (s), 1250 (s), 1140 (s), 720 (m); MS (EI) (*m*/*z*, %): 303 (M+, 9), 105 (73), 70 (29), 57 (100); HRMS: 303.1916 (Calcd for $C_{17}H_{25}N_3O_2$, 303.1947).

4.2.4. *tert*-Butyl 4,11b-dimethyl-8,9,10,11,11a,11b-hexahydro-6*H*-benzo[*e*]pyrido[1,2-*c*][1,2,3]triazine-6-carboxylate (2d). Yellow crystal, 58%; mp 85.5–86.0 °C (recryst. from hexane); ^{1}H NMR ($CDCl_3$) δ: 6.07 (dt, J=6.5, 1.5 Hz, 1H), 5.98 (dd, J=9.5, 6.0 Hz, 1H), 5.81 (d, J=6.0 Hz, 1H), 3.85 (m, 1H), 2.74 (dd, J=10.0, 2.5 Hz, 1H), 2.50 (dt, J=10.0, 3.0 Hz, 1H), 1.97 (s, 3H), 1.75 (m, 4H), 1.54 (s, 9H), 1.30 (m, 2H), 1.16 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 158.80, 150.56, 132.59, 130.65, 126.00, 122.33, 81.19, 65.29, 56.34, 40.07, 28.29, 25.54, 25.28, 23.74, 16.97, 16.47; IR (KBr) cm^{-1}: 2900 (m), 1700 (s), 1560 (w), 1440 (m), 1400 (m), 1360 (m), 1320 (s), 1230 (m), 1150 (s), 1090 (s), 730 (w); MS (EI) (*m*/*z*, %): 317 (M$^+$, 16), 217 (8), 105 (100), 84 (45), 57 (66); HRMS: 317.2123 (Calcd for $C_{18}H_{27}N_3O_2$, 317.2103); Anal. Calcd for $C_{18}H_{27}N_3O_2$: C, 68.11; H, 8.57; N, 13.24. Found: C, 68.35; H, 8.44; N, 13.42.

4.2.5. *tert*-Butyl 3,4a,6,8-tetramethyl-4,4a-dihydrobenzo-[*d*][1,2,3]triazine-2(3*H*)-carboxylate (2e). Brown oil, 65%; ^{1}H NMR ($CDCl_3$) δ: 6.03 (t, J=1.5 Hz, 1H), 5.45 (br s, 1H), 3.55 (d, J=13.0 Hz, 1H), 3.22 (d, J=13.0 Hz, 1H), 2.51 (s, 3H), 2.07 (d, J=1.0 Hz, 3H), 1.79 (d, J=1.5 Hz, 3H), 1.56 (s, 9H), 1.13 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 161.19, 152.49, 132.26, 130.68, 130.19, 128.66, 81.62, 63.88, 40.47, 33.39, 28.25, 27.15, 20.99, 16.47; IR (neat) cm^{-1}: 2980 (s), 2910 (s), 1730 (s), 1715 (s), 1570 (w), 1455 (m), 1410 (m), 1390 (m), 1370 (m), 1350 (m), 1320 (s), 1250 (m), 1140 (m), 1080 (m), 1030 (w), 980 (w), 910 (w), 860 (w), 800 (w), 750 (w); MS (EI) (*m*/*z*, %): 291 (M$^+$, 22), 191 (19), 176 (43), 147 (17), 133 (58), 119 (19), 91 (18), 77 (9), 57 (100), 41 (16); HRMS: 291.1940 (Calcd for $C_{16}H_{25}N_3O_2$, 291.1947).

4.2.6. *tert*-Butyl 3-ethyl-4,4a,6,8-tetramethyl-4,4a-dihydrobenzo[*d*][1,2,3]triazine-2(3*H*)-carboxylate (2f). Brown oil, 43% as a major product; ^{1}H NMR ($CDCl_3$)

δ: 6.14 (t, J=1.5 Hz, 1H), 5.55 (br s, 1H), 3.12 (d, J=7.0 Hz, 1H), 2.54 (m, 2H), 2.09 (br s, 3H), 1.82 (d, J=1.5 Hz, 3H), 1.53 (s, 9H), 1.27 (d, J=1.5 Hz, 3H), 0.98 (t, J=7.5 Hz, 3H), 0.92 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 167.83, 153.70, 133.10, 131.99, 130.55, 127.16, 80.63, 48.53, 38.59, 28.32, 21.16, 20.20, 16.71, 16.15, 12.11; IR (neat) cm^{-1}: 2950 (m), 2200 (w), 1710 (s), 1540 (w), 1450 (m), 1360 (s), 1320 (s), 1250 (m), 1140 (s), 910 (w), 720 (m); MS (EI) (*m*/*z*, %): 319 (M^+, 10), 218 (6), 147 (29), 119 (100), 72 (29),57 (59); HRMS: 319.2233 (Calcd for $C_{18}H_{29}N_3O_2$, 319.2260).

4.2.7. *tert*-Butyl 7,9,10a-trimethyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]triazine-5(10a*H*)-carboxylate (2g). Brown oil, 85%; ^{1}H NMR ($CDCl_3$) δ: 5.85 (t, J=1.5 Hz, 1H), 5.43 (br s, 1H), 3.86 (dt, J=8.8, 2.5 Hz, 1H), 3.23 (dd, J=9.5, 7.5 Hz, 1H), 3.08 (m, 1H), 2.16 (m, 2H), 2.05 (d, J=1.0 Hz, 3H), 1.88 (m, 2H), 1.76 (d, J= 1.5 Hz, 3H), 1.58 (s, 9H), 1.07 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 152.01, 150.01, 131.40, 129.22, 127.65, 126.91, 81.72, 55.43, 53.47, 37.00, 28.05, 23.21, 21.18, 19.67, 16.56; IR (neat) cm^{-1}: 2900 (s), 2200 (w), 1700 (s), 1560 (m), 1440 (s), 1320 (br s), 1140 (br s), 940 (w), 910 (m), 850 (w), 800 (w), 720 (s); MS (EI) (*m*/*z*, %): 317 (M^+, 14), 216 (3), 119 (100), 70 (30), 57 (83); HRMS: 317.2123 (Calcd for $C_{18}H_{27}N_3O_2$, 317.2103).

4.2.8. *tert*-Butyl 2,4,11b-trimethyl-8,9,10,11,11a,11b-hexahydro-6*H*-benzo[*e*]pyrido[1,2-*c*][1,2,3]triazine-6-carboxylate (2h). Brown oil, 63%; ^{1}H NMR ($CDCl_3$) δ: 5.95 (t, J=1.5 Hz, 1H), 5.50 (br s, 1H), 3.85 (m, 1H), 2.69 (dd, J=10.0, 2.5 Hz, 1H), 2.48 (dt, J=10.5, 3.0 Hz, 1H), 1.97 (s, 3H), 1.80 (d, J=1.5 Hz, 3H), 1.75 (m, 4H), 1.54 (4s, 9H), 1.31 (m, 2H), 1.11 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 158.98, 150.59, 130.28, 129.76, 127.18, 81.11, 65.67, 56.40, 39.71, 28.31, 25.59, 25.33, 23.81, 21.58, 17.08, 16.83; IR (neat) cm^{-1}: 2900 (m), 1700 (s), 1560 (w), 1440 (m), 1400 (m), 1360 (m), 1310 (s), 1260 (m), 1160 (m), 1100 (m), 740 (m); MS (EI) (*m*/*z*, %): 331 (M^+, 20), 230 (8), 119 (100), 84 (41), 57 (51); HRMS: 331.2270 (Calcd for $C_{19}H_{29}N_3O_2$, 331.2260).

4.2.9. *tert*-Butyl 3,4a-dimethyl-4,4a-dihydronaphtho[1,2-*d*][1,2,3]triazine-2(3*H*)-carboxylate (4). Yellow oil, 93%; ^{1}H NMR ($CDCl_3$) δ: 7.98 (m, 1H), 7.32 (m, 2H), 7.10 (m, 1H), 6.42 (d, J=10.0 Hz, 1H), 5.89 (d, J=10.0 Hz, 1H), 3.56 (d, J=14.0 Hz, 1H), 3.41 (d, J=14.0 Hz, 1H), 2.69 (s, 3H), 1.59 (s, 9H), 1.22 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 155.15, 152.04, 136.94, 133.40, 129.89, 129.74, 128.22, 126.49, 125.28, 124.76, 82.01, 61.85, 40.31, 31.86, 28.25, 26.45; IR (neat) cm^{-1}: 3000 (s), 1700 (s), 1610 (s), 1580 (w), 1480 (m), 1370 (s), 1310 (s), 1250 (m), 1170 (m), 1140 (s), 1100 (s), 910 (w); MS (EI) (*m*/*z*, %): 313 (M^+, 3.8), 212 (35), 198 (16), 182 (10), 168 (16), 155 (100), 141 (85), 128 (6.3), 115 (27), 115 (28), 89 (3.1), 63 (3.1), 57 (59), 51 (2.5), 41 (2.4); HRMS: 313.1759 (Calcd for $C_{18}H_{23}N_3O_2$, 313.1790).

4.3. X-ray crystallographic analysis

Data of compound **2d** was taken on a RigakuAFC5R diffractometer with graphite-monochromated Mo Kα radiation (k=0.71069 Å). The structure of **2d** was solved by direct methods with SAPI91.[16] Full-matrix least-squares refinement was employed with anisotropic thermal parameters for all non-hydrogen atoms. All calculations were performed using the teXsan[17] crystallographic software package of Molecular Structure Corporation. An ORTEP drawing of compound **2d** is shown in Figure 1.

4.3.1. Crystal data for 2d. Monoclinic, space group $P2_1/n$, a=9.988(5), b=9.321(4), c=19.961(3) Å, V=1850(1) Å^3, Z=4, μ(Mo Kα)=0.75 cm^{-1}, F(000)=688, D_{calcd}=1.139 g/cm^3, crystal dimensions: 0.30×0.30×0.40 mm. A total of 4761 reflections (4511 unique) were collected using the $\omega-2\theta$ scan technique to a maximum 2θ value of 55°, and 1291 reflections with $I>3\sigma(I)$ were used in the structural determination. Final R and wR values were 0.045 and 0.042, respectively. The maximum and minimum peaks in the difference map were 0.14 e$^-$ Å^{-3}.

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