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FORMATION AND AMINATION OF DIBENZ[*b, f,* -1]AZAPENTALENE DIANION

ATTEMPTED SYNTHESIS OF DIBENZ[*b, f,*-1]AZAPENTALENE

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Abstract—Dibenz[*b,f,*-1]azapentalene dianion (**3**) was allowed to react with N,N diethyl - O - mesitylenesulfonylhydroxylamine (**4**) in order to obtain N,N - diethyl - 5,10 - dihydroindeno[1,2 - *b*] - indol - 10 - amine (**11**). The available data indicated that electron transfer processes were involved in the formation of **11**. Attempts to obtain dibenz[*b, f,* -1]azapentalene (**1**) from **11** by Hofman elimination or by the reaction of **11** with trifluoroacetic acid were unsuccessful.

IN SPITE of efforts over the past 60 yr, pentalene has eluded the grasp of synthetic chemists.[1] The extreme instability of this molecule is attested by the tendency of 1 - methylpentalene[2] to dimerize at −140°. Pentalene derivatives that are stable at room temperature owe their existence to electronic[3] and steric[4] effects. Studies of these stable systems have contributed greatly to our understanding of one aspect of carbocyclic pi-bonding, particularly in the formulation of the concept of antiaromaticity.[5] In order to explore the concept of heterocyclic antiaromaticity, the first known 1 - azapentalene, namely 10 - phenyldibenz[*b, f,* -1]azapentalene was synthesized. This compound displayed dramatic chemical and physical properties.[6] In order to further our understanding of antiaromaticity as applicable to this heterocyclic system, the 1 - aza analog of the stable dibenzo[*b, f*]pentalene[7] was sought. An attempt at the synthesis of dibenz[*b, f,* -1]azapentalene (**1**) is the subject of this report.

Since dibenzo[*b, f*]pentalene has been obtained[8] by a double Hofmann elimination from 4b,5,9b,10 - tetrahydro - N,N,N′,N′ - tetramethylindeno[2,1-*a*]indene - 5,10 - diamine, the synthesis of the corresponding aza analog (**1**) starting with N,N - diethyl - 5,10 - dihydroindeno[1,2-*b*]indol - 10 - amine (**11**) appeared viable. Dibenzopentalene polymerizes in boiling benzene and in dilute aqueous acids. It is stable, however, in concentrated acid.[7] Apparently the molecule polymerizes in acid by the attack of a neutral molecule on a protonated species. In strong acids, the unavailability of neutral molecules prevent polymerization. Indeed, this is what was found in the case of 10 - phenyldibenz[*b, f,* -1]azapentalene.[9a] Formation of a stable salt of dibenz[*b, f,* -1]azapentalene by proton assisted elimination of the diethylamino moiety of **11** in the presence of strong acid was also envisioned.

Amination of dibenz[*b, f,* -1]azapentalene dianion (**3**) with **4** resulted in the formation of **11**. N,N - diethyl - O - mesitylenesulfonylhydroxylamine (**4**), a reagent which "electrophilically" aminates carbanions was prepared by modification of a literature procedure.[10] The dianion (**3**) formed by the action of butyllithium on 5,10 - dihydroindeno[1,2-*b*]indole (**2**) in tetrahydrofuran (THF) containing tetramethylethylenediamine (TMEDA), was allowed to react with **4**. The products isolated included starting material **2** 34%, **11** 43% and the dimer (**10**) 0.7%.

The following facts were associated with this reaction:

(a) The dianion (**3**) was formed in quantitative yield (the methylene proton PMR signal of the product obtained by quenching a THF solution of **3** with D_2O was half the relative intensity of the corresponding signal obtained from the product of H_2O addition).

(b) The red color of the dianon (**3**) was discharged shortly after exposure to **4**.

(c) Without the use of TMEDA, the yield of **11** dropped to 22% with a corresponding increase in the formation of **2**.

(d) The yield of the aminated product (**14**) resulting from the N - protected monoanion (**13**) in THF without the benefit of TMEDA was 20%.[11]

Although nucleophilic displacement cannot be ruled out, evidence obtained so far indicated that the reaction proceeded by electron transfer. Since the dianion (**3**) formed in quantitative yield and as its red color discharged shortly after exposure to **4**, the reaction medium appears to be a hydrogen donor. The dianion (**3**) was stable in the THF/TMEDA solvent combination. The use of TMEDA which enhances the basicity of the dianion, resulted in an increase yield of the aminated product (**11**), and a lower yield of **2**. Hence it appears that the origin of **2** (which formed in substantial amount [34%]) is not the result of proton abstraction by **3** from **4**, although this possibility cannot be ruled out.

The free dianion is expected to exist predominantly in the resonance form **3**. As the indenyl anion has a greater aromatic stabilization energy than the indolyl anion,[12] one would expect electron transfer to take place from the heterocyclic ring rather than from the 5 - membered carbocyclic ring. However, the Li cation would be expected to strongly coordinate with the heteroatom, a factor which apparently leads to preferential electron transfer from the carbocyclic ring. Consequently the yield of product resulting from amination at C-10 is not increased by employing the monoanion derived from N - t - butoxymethyl - 5,10 - dihydroindeno[1,2-*b*]indole (**13**), where electron transfer from the heterocyclic ring is unlikely. The probable course of the reaction is outlined in Scheme 1.

After the transfer of an electron from the charged carbocyclic ring of **3** to **4** (the latter is expected to be a

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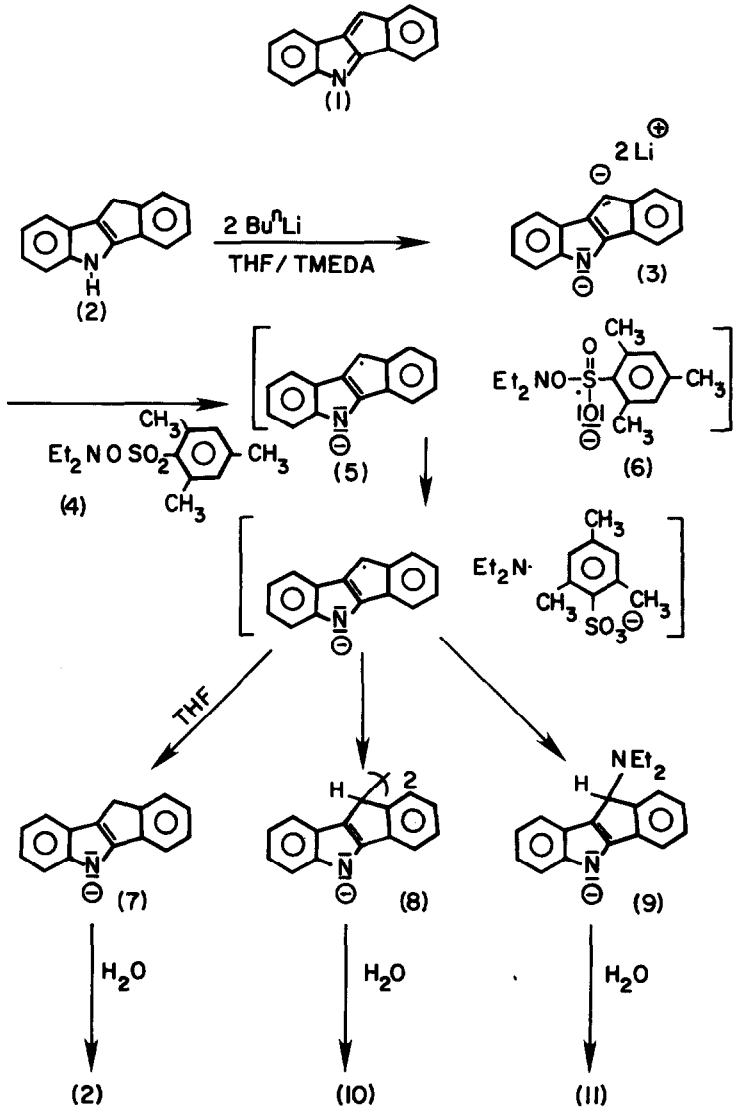


Scheme 1.

good electron acceptor[13]) the radical ion (**5**) can abstract a proton from the solvent to give **2**, or couple with the diethylamino radical generated by the decomposition of the N,N - diethyl - O - mesitylenesulfonyl radical anion.

TMEDA coordinates with the Li cation associated with the carbocyclic ring, making that carbanion a stronger base, and thus facilitating electron transfer.[13] The presence of TMEDA also presumably hinders hydrogen abstraction by **5** from THF, thereby fostering coupling with the diethylamino radical in the solvent cage. The radical anion (**5**) dimerizes to a small extent to give 0.7% of 5,5',10,10' - tetrahydro - 10,10' - biindeno[1,2,-*b*]indole (**10**).

The N atom bonded to C-10 of **11** could easily be quarternized by simply dissolving the free amine in methyl iodide and then precipitating the salt (**15**) from the solution by the addition of anhydrous ether. Dibenz[*b*, *f*, -1]azapentalene was expected to form from **15** via the zwitterion (**17**). In an attempt to achieve this end and to trap **1** as its addition products with potassium t - butoxide, a suspension of **15** in THF was allowed to react with an excess of the latter reagent. This resulted in the isolation of **11**. Apparently the instability induced by steric crowding at the quarternized nitrogen makes **15** a good methylating agent. This is again apparent in the inability of **11** to be alkylated by ethyl iodide. The addition of anhydrous ether to a solution of **11** in ethyl iodide, which was kept for 2 hr at room temperature, yielded only traces of precipitate.

Indeed, steric effects prevented the protonation of **11** by trifluoroacetic acid. The PMR spectrum of **11** in trifluoracetic acid (Table 1) revealed that the C-10 hydrogen signal does not undergo any significant shift downfield when compared with the corresponding signal obtained from a solution of **11** in $CDCl_3$. A shift downfield is expected only if protonation occurs.[14] Rotation about the C-10–N bond is restricted due to solvation of the diethylamino group. This makes the two Et groups nonequivalent, and their methylene protons diasteriotopic.

Bubbling anhydrous hydrogen chloride through an ethereal solution of **11** leads to precipitation of the

Table 1. ^{1}H NMR data

	δ (ppm)	APPEARANCE	ASSIGNMENT
(11) in CF_3CO_2H	1.02,1.13,1.26 1.37 1.48 1.60,1.70,1.82	triplet (1:2:1) singlet singlet triplet (1:2:1)	2 CH_3
	2.36-3.05	broad,unresolved triplet	CH_2
	3.17-4.04	broad,unresolved triplet	CH_2
	4.80	singlet	C_{10}-H
	7.36,7.53	broad singlets	Aromatic H
	8.90-9.74	broad	N-H of pyrrole
(11) in CF_3CO_2H after 3 days at room temp.	1.23	triplet J=7Hz	2 CH_3
	3.12	sextet (1:5:10:10:5:1) J=7Hz	2 CH_2
	3.96-4.44	broad	-
	5.27-8.7	broad	-
(16) in DMSO-d_6	0.77-1.43	broad, unresolved triplet	CH_3
	1.43-2.1	broad, unresolved triplet	CH_3
	2.16-2.90	broad	CH_2 (obscured by DMSO-d_5)
	2.90-4.00	broad	CH_2 (obscured by H_2O in solvent)
	5.70	singlet	C_{10}-H
	6.83-8.20	multiplet	7 Aromatic H
	8.53	doublet J=7Hz	C_1-H

hydrochloride salt (**16**). The PMR spectra of **16** and **11** in trifluoroacetic acid were identical indicating dissociation of **16** to **11**. In deuterated dimethyl sulfoxide, however, the smaller chloride ion allowed the existence of the ion pair (Table 1). Again, rotation about the C–10–N bond is restricted and the C-10 hydrogen signal is shifted 0.85 ppm downfield. The C-10 hydrogen and the hydrogen on the protonated nitrogen are eclipsed, or nearly so, as no coupling between these hydrogens is apparent.[14]

After allowing a trifluoroacetic acid solution of **11** to stand three days at room temperature, the diethylamine eliminated is easily recognized in the PMR spectrum (Table 1). The dibenz[*b,f*,-1]azapentalene formed apparently undergoes subsequent reactions as the aromatic region of the original spectrum is replaced with a broad, poorly resolved absorption. In contrast the PMR spectrum of 10 - phenyldibenz[*b,f*,-1]azapentalene in trifluoroacetic acid consisted of sharp, well defined signals.[9b] It appears that the loss of the elements of diethylamine resulted in oligomerization, if not polymerization, of the intermediate azapentalene which apparently is not stabilized as a salt. Mass spectral analysis of the isolated crude indicated the presence of a dimeric substance (*m/e* 479) in addition to faint peaks corresponding to higher molecular weights (*m/e* 682, 683, 684). Materials with even higher molecular weight would not be observed due to a lack of volatility. No peak corresponding to dibenz[*b,f*,-1]azapentalene (**1**) (*m/e* 203), its dimer or its addition products with water (*m/e* 221) could be observed. The IR spectrum of the crude was devoid of absorption in the C=N stretching region. Although the products of this reaction have not been identified, the presence of dibenz[*b,f*,-1]azapentalene has been excluded.

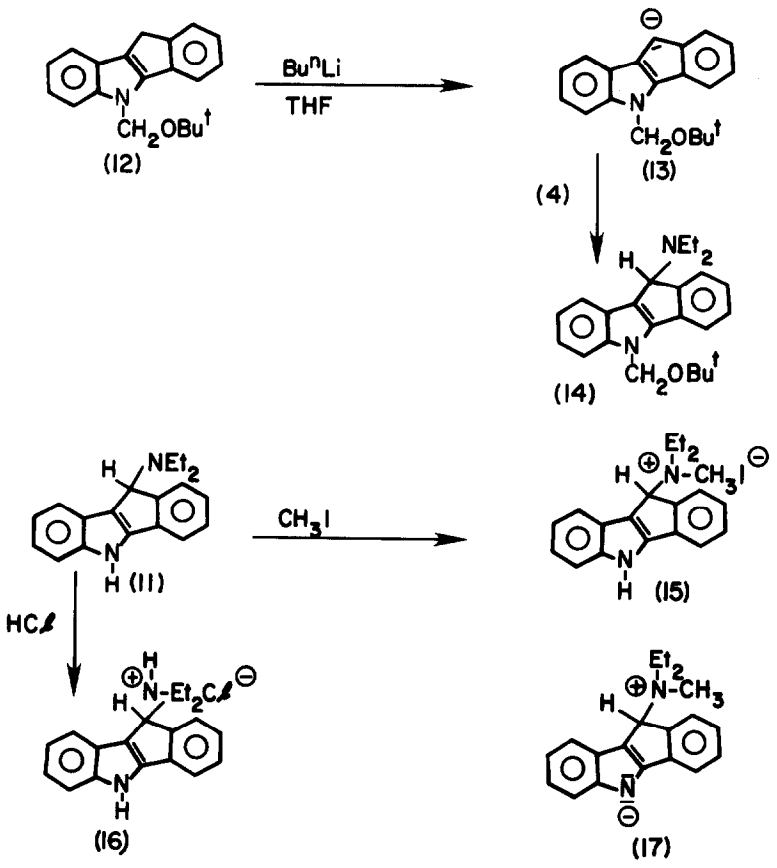
EXPERIMENTAL

PMR spectra were recorded on a Varian EM360A 60 MHz spectrometer. Chemical shifts are given in ppm form TMS. IR spectra were obtained on a Beckman 1R 33 spectrophotometer. Data was also obtained at the Mass Spectral Facility of Cornell University and on a DuPont 21-490 mass spectrometer.

Mesitylenesulfonyl chloride (Aldrich) was purified by dissolving it in a minimum amount of $CHCl_3$ (20.0g in 20ml of $CHCl_3$) and then adding 10 volumes of petroleum ether (b.p. 30–60°). A small quantity of suspended material was filtered out.

The filtrate was reduced in volume to *ca* 15 ml before cooling (ice bath) to crystallize. Recrystallization from $CHCl_3$ gave white crystals (m.p. 53.5–56.5°).

N,N - Diethylhydroxyl amine, triethylamine, tetramethylethylenediamine and methylene chloride were distilled from calcium hydride under Ni. THF was dried by distillation from sodium benzophenone ketyl.



Scheme 2.

5,10 - *Dihydroindeno*[1,2-*b*]*indole* (**2**). This compound was prepared as previously described from 1 - indanone and phenylhydrazine in refluxing methanolic HCl (m.p. 249–255° dec. lit.[15] 227–228°). IR (nujol): 3400(s), 1306(m), 1247(m), 761(m), 741(s) and 723 cm^{-1} (m). ^{1}H NMR(DMSO-d_6): 3.68(s, 2) and 6.9–8.0 (m,9).

N,N - Diethyl - O - mesitylenesulfonylhydroxylamine (**4**). A soln of mesitylenesulfonyl chloride (76.8 mmol, 16.81 g) in 50 ml CH_2Cl_2 was added dropwise over 45 min to a stirred soln of N,N - diethylhydroxylamine (90.0 mmol, 9.25 ml) and Et_3N (15 ml) in 50 ml CH_2Cl_2 maintained at −25° under N_2. A white ppt appeared during the course of the reaction. The mixture was stirred at −25° for a total time of 2.5 hr.

At the end of this period, the mixture was washed with 100 ml ice-cold water and the water layer was extracted with cold ether (2 × 100 ml). The combined organic layer, which was always kept cold (ice bath), was washed with ice-cold water (3 × 100 ml). After drying ($MgSO_4$), the organic layer was cooled in a dry-ice bath for a few min to yield white crystals. These were quickly filtered off with suction (water aspirator) and then washed with 25 ml ice-cold ether. After drying *in vacuo* (0.1 mm) for 2 hr at room temp., the product **4** weighed 12.1 g (58%, m.p. 75° dec). IR (nujol): 1600(m), 1565(m), 1195(s), 1180(s), 1160(m), 1060(m), 1040(m), 840(s), 790(s) and 665 cm^{-1}(s). ^{1}H NMR: 0.94(t,6,J = 7 Hz), 2.95(q,4,J = 7 Hz), 2.67(s,6), 2.34(s,3) and 7.04(s,2). Attempted recrystallization from ether (lit.[10] m.p. 68–69° from ether) led to discoloration and oiling out of **4**. Pure **4** can be prepared as described above provided that starting materials are purified as suggested. N,N - diethyl - O - mesitylenesulfonylhydroxylamine decomposes on standing at room temp. However, when kept in a freezer, a sample of **4** stored in a plastic bag containing drierite showed no change in its decomposition point after 6 weeks.

Formation of dibenz[*b,f*,-1]*azapentalene dianion* (**3**) *and its subsequent reaction with N,N - diethyl - O - mesitylenesulfonylhydroxlamine* (**4**). Under N_2, n - BuLi (67.5 mmol, 30 ml of a 2.25 M soln in hexane) was added dropwise to a cooled soln (ice-bath) of 5,10 - dihydroindeno[1,2-*b*]indole (32.1 mmol, 6.6 g) in 200 ml anhydrous THF and 20 ml of anhyd tetramethylethylenediamine. After the addition was complete, the contents of the reaction flask (i.e. the red soln of the dianion and the yellow ppt of the dilithium salt) was stirred for 45 min. at room temp.

The reaction vessel was then cooled to −78° and solid N,N-diethyl - O - mesitylenesulfonylhydroxylamine (39.7 mmol, 8.7 g) was added in one portion. On removal of the cooling bath after 5 min, the red color of the dianion was soon discharged. The reaction vessel was gradually allowed to warm up to room temp., and the stirring was continued overnight.

After the addition of ether (150 ml) the organic layer was washed with water (2 × 100 ml), followed by extraction with 2N HCl (2 × 60 ml). On standing, a white ppt appeared in the aqueous acid soln. This ppt was filtered off, suspended in 2N NaOH (100 ml) and extracted with ether (150 ml). Most of the solid dissolved leaving only a small quantity of insoluble material. The ether was then washed with water (3 × 100 ml), dried ($MgSO_4$), and evapourated to yield (11) as a brownish–pink solid (43% 3.8 g, m.p. 126.0–126.5° dec). Recrystallization from light petroleum (b.p. 30–60°) gave tan crystals of the same m.p. Calc'd: for $C_{19}H_{20}N_2$: C, 82.56; H, 7,28; N, 10.13. Found: C, 82.81; H, 7.29; N, 9.93. IR (nujol): 3405(s), 1305(s), 760(s) and 750 cm^{-1}(s). ^{1}H NMR ($CDCl_3$): 1.08 (t,6,J = 7 Hz), 2.58 (q,4,J = 7 Hz), 4.87 (s,1) 7.03–7.91 (m,8) and 8.2 (s,br,1).

The solid insoluble in the ether layer was boiled briefly in EtOAc, then filtered hot to leave the hydrochloride salt (**16**) as an off-white residue. IR(KBr): 3690–2000 (s,br, max at 3410, 3110, 2580 and 2490 cm^{-1}), 1450(s), 1310(m) and 730 cm^{-1}(s). Compound **11** could be liberated by treatment of a suspension of **16** in anhyd THF with t - BuOK.

Careful neutralization of the HClaq layer by addition of NaOH pellets yielded a brown oil which could be isolated by ethereal extraction. This material which could have contained products of amination at the 5 and 9b positions of the indenoindole nucleus in addition to more of **11** was not analyzed.

The original ether layer which was extracted with HClaq was washed with water, dried ($MgSO_4$), and evapourated to an off-white solid which was taken up in 50 ml of hot EtOAc. The hot soln was filtered to leave 0.05 g of an insoluble white solid. The filtrate was evapourated to yield 2.24 g (34%) of **2**. The insoluble material was found to be 5,5', 10,10' - tetrahydro - 10,10-biindeno[1,2-*b*]indole (**10**),[9c] m.p. 360–361° dec IR(nujol): 3400(s) and 740 cm^{-1}(s). ^1H NMR (DMSO-d_6): 4.9 (s,2) and 5.2–8.5 (m,18). MS (70eV, electron impact, *m/e* [%] given: 409 (6), 408 (18), 406 (5), 205 (33), 204 (100) and 203 (33).

N,N - Diethyl - 5,10 - dihydro - N - methylindeno[1,2-b]indol - 10 - aminium iodide (**15**). Compound **11** (1.66 mmol, 0.46 g) was dissolved in 5 ml MeI and the soln was stirred under N_2 for 3 hr at room temp. The methiodide (**15**) precipitated from the soln upon the addition of anhyd ether. The white ppt was filtered off, washed with anhyd ether and dried in air (0.44 g, 63% m.p. 133–135° dec). IR (nujol): 3210(s) and 750 cm^{-1}(s).

Reaction of N,N - diethyl - 5,10 - dihydro - N - methyl - indeno[1,2-b]indol - 10 - aminium iodide (**15**) *with excess potassium t - butoxide.* t - BuOK (2.85 mmol, 0.32 g) was added to a stirred suspension of **15** (0.95 mmol, 0.4 g) in 5 ml anhyd THF under N_2. After stirring for 3 hr at room temp., ether was added to the reaction flask, the organic layer was washed with water, dried ($MgSO_4$), and was evaporated to a crude solid (0.2 g, 78%). Spectral data (IR, ^1H NMR) of this substance was identical with that of **11**.

N,N - Diethyl - 5,10 - dihydroindeno[1,2-b]indol - 10 - amine hydrochloride (**16**). Compound **11** (0.4 g, 1.45 mmol) was dissolved in 20 ml anhyd ether. Anhyd HCl was then bubbled into the ethereal soln to precipitate **16** as a white solid. The ppt was filtered off, washed with anhyd ether, and dried in air (0.4 g, 88%, m.p. 153° dec).

Reaction of N,N - diethyl - 5,10 - dihydroindeno[1,2-b]indol - 10 - amine with trifluoroacetic acid. Compound **11** (0.3 g) was dissolved in trifluoroacetic acid (0.5 ml) and the resulting soln was stirred under N_2 for 3 days at room temp. At the end of this period CH_2Cl_2 (30 ml) was added. The soln was then washed repeatedly with water, dried ($MgSO_4$), and the solvent was removed at room temp (vacuum pump) to leave a brown solid (0.25 g). IR(KBr): 3430(s), 3060(w), 2980(w), 1615(w), 1445(s), 1365(m), 1340(m), 1305(m) and 750 cm^{-1}(s). MS (70eV, chemical ionization with methane, *m/e* [%] given): 204(5.1), 205(13.2), 206(16.9), 220, 234, 298(traces), 407(5.8), 408(4.4), 409(2.9), 451(5.8), 452(5.8), 464(9.5), 479(82.3), 480(100), 508(7.3) and 682, 683, 684(traces).

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