Synthesis and Properties of Bis(cyclopropylphenyl)cyclopropenones and the Tris(*p*-cyclopropylphenyl)cyclopropenium Ion

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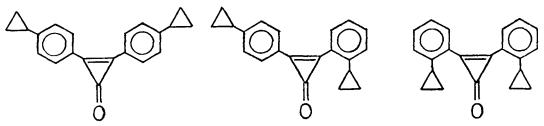
The reaction of trichlorocyclopropenium tetrachloroaluminate with cyclopropylbenzene has been found to readily afford the disubstitution products, bis(*p*-cyclopropylphenyl)- (**1a**), (*p*-cyclopropylphenyl) (*o*-cyclopropylphenyl)-, and bis(*o*-cyclopropylphenyl)cyclopropenones, each of which has been separated and fully characterized spectroscopically. The tris(*p*-cyclopropylphenyl)cyclopropenium ion (**2**) could not be obtained by the direct trisubstitution of the trichlorocyclopropenium ion with cyclopropylbenzene, but has been synthesized *via* two other routes starting from cyclopropenone **1a**. The UV and ^{13}C NMR spectral data of the cation **2** indicated the conjugative interaction of the *para*-cyclopropyl group with the cyclopropenium ring. However, the cation-stabilizing effect of the *para*-cyclopropyl group, as shown by the pK_{R^+} value (3.23 in 23% ethanol) for **2**, is much smaller than in the case of the tris(*p*-cyclopropylphenyl)methyl cation. This has been interpreted in terms of the decrease in delocalization of the positive charge to the *para*-position of the cation **2**, when compared with the triarylmethyl analogue.

The smallest-ring member of the aromatic halocarbon, the trichlorocyclopropenium ion ($C_3Cl_3^+$), was first synthesized by Tobey and West,[1a] and found to react with various aromatic rings resulting in stepwise electrophilic substitution.[1b] Recently this reaction was successfully applied to the syntheses of new cyclopropenium ions stabilized by non-benzenoid- or heteroaromatic substituents such as ferrocene,[2] azulene,[3] and thiophene rings.[4] Among the substituted benzenes, those carrying the strongly activating groups such as methoxyl, hydroxyl, and dialkylamino groups react with $C_3Cl_3^+AlCl_4^-$ to give the trisubstituted product, *i.e.* the triarylcyclopropenium ion,[1b,5] whereas the unsubstituted and weakly activated benzenes such as fluorobenzene and toluene give only the disubstituted cyclopropenones.[6]** Since the cyclopropyl group is expected to exert conjugative stabilization upon the cationic intermediate formed during the reaction,*** it was of interest to establish whether such an effect could lead to the trisubstitution of $C_3Cl_3^+$ with cyclopropylbenzene. Also having been interested in the stabilizing effect of the cyclopropyl group upon the triarylcyclopropenium ion which may be prepared by this reaction, we examined the reaction of $C_3Cl_3^+$-$AlCl_4^-$ with cyclopropylbenzene.

Results and Discussion

Bis(cyclopropylphenyl)cyclopropenones. The reaction of $C_3Cl_3^+AlCl_4^-$ with cyclopropylbenzene was examined in dichloromethane in the temperature range −60 to 40 °C. When two molar equivalents of cyclopropylbenzene were employed the disubstitution reaction occurred smoothly at −10 °C yielding a mixture of the isomeric bis(cyclopropylphenyl)cyclopropenones (**1a**, **1b**, and **1c**) after hydrolysis. Complete separation of the isomers was effected by the use of thin-layer chromatography. The R_f values of each component (**1a**, 0.14; **1b**, 0.34; **1c**, 0.64 : over silica gel developed with benzene–ether (4 : 1)) reflect the extent of molecular polarization, the *p,p*-isomer (**1a**) being the least developed due to the greatest polarization with two cyclopropyl groups located farthest away from the carbonyl group. In a representative run, the yield of the cyclopropenones was 31.2% for **1a**, 47.2% for **1b**, and 7.4% for **1c**. Assuming that the *ortho*/*para* reactivity ratio does not change between the first and the second substitutions of $C_3Cl_3^+$, it has been estimated from the yields of **1a** and **1b** that the *para*-position of cyclopropylbenzene is approximately 2.6 times more reactive to the electrophilic attack of $C_3Cl_3^+$ than the *ortho*-position. The decrease in the yield of **1c** (7.4%) to approximately half the calculated value (18%) is



1a **1b** **1c**

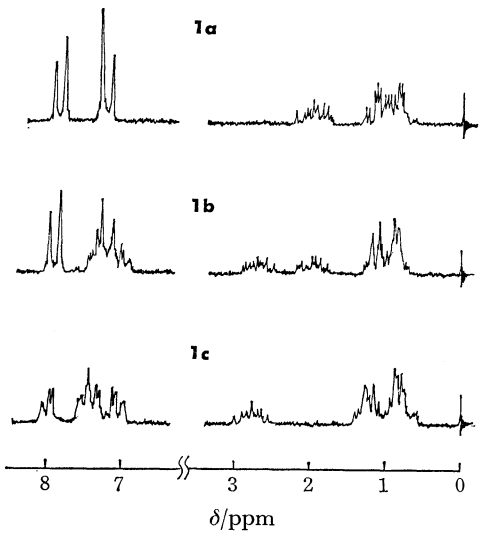


Fig. 1. ^1H NMR Spectra of the cyclopropenones **1a**, **1b**, and **1c**.

** The σ_p^+ values, which express the ability of the substituent to stabilize the cationic intermediate, are −0.778 for OCH_3, −0.92 for OH, −1.7 for NMe_2, −0.073 for F, and −0.311 for CH_3.[7]

*** The σ_p^+ value for the cyclopropyl group has been reported as −0.462.[8]

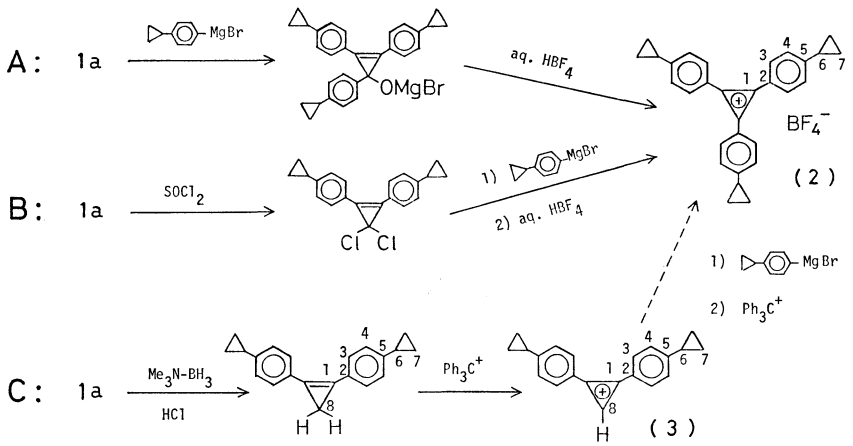
Table 1. Physical and spectral properties of the bis(cyclopropylphenyl)-cyclopropenones, **1a**, **1b**, and **1c**

Compd	Mp °C	IR ν(KBr) cm^{-1}	UV λ_{max}^{EtOH} nm (log ε)	^1H NMR δ ($CDCl_3$) ppm
1a	142.6—144.5	1850 1610	277 sh(4.45), 295 (4.59), 301 sh(4.50), 313 (4.52),	7.83 (d, 4H, *o*-H), 7.22 (d, 4H, *m*-H), 2.00 (m, 2H, methine), 1.3—0.8 (m, 8H, CH_2)
1b	83.5— 85.0	1845 1605	294 sh(4.30), 307 (4.40), 325 (4.38), 337 sh(4.32)	7.88 (d, 2H, *o*-H), 7.20 (m, 6H, aromatic), 2.70 (m, 1H, methine), 1.95 (m, 1H, methine), 1.3—0.7 (m, 8H, CH_2)
1c	120.0—121.0	1850 1600	289 (4.23), 312 (4.17), 324 (4.15), 341 sh(4.08)	8.0—7.0 (m, 8H, aromatic), 2.77 (m, 2H, methine), 1.3—0.7 (m, 8H, CH_2)

Table 2. Physical and spectral properties of the tris- (**2**) and the bis(*p*-cyclopropylphenyl)cyclopropenium ions (**3**)

Compd	Mp °C	IR ν(KBr)cm^{-1}	UV λ_{max}^{EtOH} nm (log ε)	^1H NMR δ ($CDCl_3$) ppm
2	>250	1410 1050	230 (4.33), 285 sh(4.25), 343 (4.84), 359 (4.84)	8.32 (d, 6H, *o*-H), 7.53 (d, 6H, *m*-H) 2.17 (m, 3H, methine), 1.30 (m, 6H, (*E*)-CH_2), 1.03 (m, 6H, (*Z*)-CH_2)[a]
3	169.0—171.0 (dec)	1415 1050	220 (4.17), 279 (4.10) 343 (4.63)	10.40 (s, 1H, C^+-H), 8.25 (d, 4H, *o*-H) 7.39 (d, 4H, *m*-H), 2.02 (m, 2H, methine), 1.25 (m, 4H, (*E*)-CH_2), 0.93 (m, 4H, (*Z*)-CH_2)

a) Taken in CD_2Cl_2.



Scheme 1.

thus ascribed to steric inhibition which operates more strongly at the second substitution step.

The physical properties of the cyclopropenones, **1a**, **1b**, and **1c**, are given in Table 1. The compounds all exhibit two broad and strong IR absorption bands at 1850 and $\approx$1610 cm^{-1}, which are diagnostic for the cyclopropenone system. The higher mp's for **1a** and **1c** are consistent with the symmetrical positions of the substituents, but stronger evidence for structure **1a**, **1b**, and **1c** is given by the ^1H NMR spectra. As is shown in Fig. 1 compound **1a** exhibits an AB quartet for the aromatic protons indicating substitution only at the *para*-position, while compound **1b** has an AB quartet plus a multiplet in the aromatic region. Furthermore, in the spectrum of **1b** one of the two cyclopropyl methine multiplets is shifted downfield, presumably due to the deshielding effect of the carbonyl group, to the same position as that of the compound **1c**, which is consistent with the assignment of **1b** and **1c** to the *o,p*- and *o,o*-isomers respectively.

*Tris(*p*-cyclopropylphenyl)cyclopropenium Ion.* In contrast to the ready formation of diarylcyclopropenones, the reaction of $C_3Cl_3^+AlCl_4^-$ with three molar equivalents of cyclopropylbenzene at low (−60 °C) or ambient temperature did not produce any evidence for trisubstitution. The reaction conducted at higher temperature (40 °C) for a prolonged time merely resulted in the formation of intractable polymeric material. Thus, attempts were made to synthesize the tris(*p*-cyclopropylphenyl)cyclopropenium ion (**2**) from cyclopropenone **1a** following the three synthetic routes shown in Scheme 1.† Methods A and B gave the tetrafluoroborate salt of the cation **2** in a low yield. On the other hand, method C afforded the bis(*p*-

† The reaction of 1,2-bis(*p*-cyclopropylphenyl)-3,3-dichlorocyclopropene with cyclopropylbenzene in the presence of silver triflate according to the method reported by Weiss *et al.*[9] afforded an inseparable mixture of the triflate (32% yield) of the cation **2** and 1,2-bis(*p*-cyclopropylphenyl)-3-(*o*-cyclopropylphenyl)cyclopropenium ion.

Table 3. ^{13}C NMR data for the triphenylcyclopropenium ion (**4**) and the tris- (**2**) and the bis(*p*-cyclopropylphenyl)cyclopropenium ions (**3**)

Cation	Chemical shift δ (CD_3CN), ppm from TMS[a]							
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
4[b]	156.7 s	121.0 s	137.0 d	131.5 d	139.6 d	—	—	—
2	152.9 s [c]	118.0 s	136.8 d	128.0 d	158.6 s	17.5 d	12.9 t	—
3	161.1 s [c]	117.0 s	137.6 d	127.9 d	160.0 s	17.6 d	13.1 t	151.6 d

a) The peak multiplicity of the off-resonance spectrum is indicated by s (singlet), d (doublet), and t (triplet). b) The numbering system is similar to that used in the cation **2**. The reported values obtained in $ClSO_3H$ are 155.4(C-1), 120.1(C-2), 135.9(C-3), 131.2(C-4), and 139.2(C-5) ppm from TMS.[10] c) The assignment of these signals to C-1, not to C-5, is made based on the fact that in the proton-coupled spectra the signals are distinctly more narrow and sharp compared with those for C-5 carbons which are apparently broadened by the long-range coupling with protons attached to the C-4 and C-6 carbons.

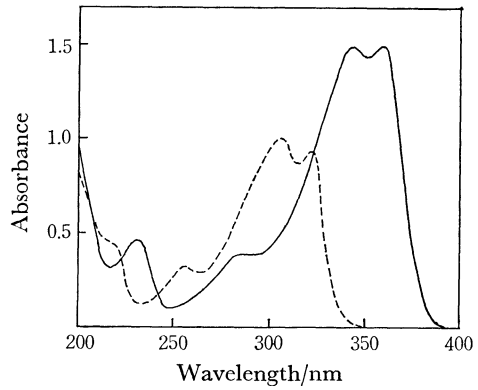


Fig. 2. UV Spectra of the tris(*p*-cyclopropylphenyl)-cyclopropenium ion (**2**, ——) and the triphenylcyclopropenium ion (**4**, ----), 2.1×10^{-5} M in CH_3CN.

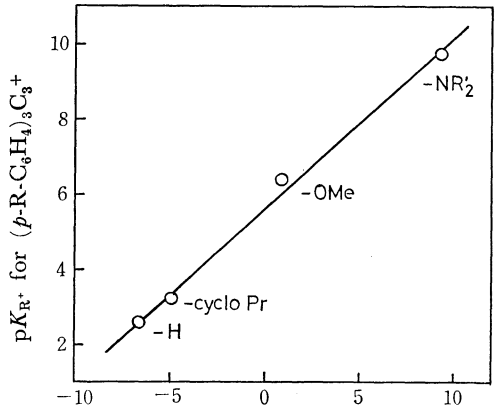


Fig. 3. Plot of the pK_{R^+} values for the *para*-substituted triarylcyclopropenium ions against those for the corresponding triarylmethyl cations. The alkyl group R′ in "$-NR'_2$" is methyl for $(p\text{-R-C}_6H_4)_3C^+$ and isopropyl for $(p\text{-R-C}_6H_4)_3C_3^+$.

cyclopropylphenyl)cyclopropenium ion (**3**) in a 59.1% overall yield, but the presence of many unfavorable side reactions in the subsequent reaction-step rendered this route impractical as a synthetic route for the cation **2**.

The spectral properties of the cations **2** and **3** are shown in Table 2. For both cations, the IR spectra exhibit broad and strong absorptions at ≈1410 cm^{-1}, which is assigned to the cyclopropenium ring stretching, and at 1050 cm^{-1} due to the tetrafluoroborate anion, while the AB quartets of the aromatic protons in the ^1H NMR spectra illustrate the presence of all the cyclopropyl substituents at the *para*-position. As shown in Fig. 2 the UV spectrum of cation **2** is quite similar to that of the unsubstituted triphenylcyclopropenium ion (**4**) in general absorption pattern, but the longer-wave absorptions of the former are bathochromically shifted by *ca.* 40 nm with an apparent increase in the absorption coefficient. This shift is regarded as a result of conjugative interaction of the *para*-cyclopropyl group with the cationic central ring. The ^{13}C NMR data shown in Table 3 allow a more quantitative estimation of the conjugative effect of the *para*-cyclopropyl group : from the difference in chemical shift for the C-1 signal between the cyclopropylsubstituted cation **2** and the unsubstituted cation **4** and the Spiesecke-Schneider correlation $\Delta\delta=160\Delta q$, the amount of the positive charge withdrawn from the cyclopropenium ring has been calculated as +0.071 or 7.3% of the amount of the positive charge (+0.969)[10] assumed to be originally present in the three-membered ring of cation **4**.

Stabilization of cation **2** resulting from the conjugative effect of the cyclopropyl group is demonstrated by the pK_{R^+} value of 3.23 (spectrophotometrical method in 23% aqueous ethanol at 25 °C) as compared with the value of 2.60[11] determined for the unsubstituted cation **4** in our laboratory. In the case of the triphenylmethyl cation system, substitution with three *para*-cyclopropyl groups has been reported to raise the pK_{R^+} value from −6.6 for the unsubstituted cation to −4.9.[12] Thus, in order to compare the effectiveness of various *para*-substituents on the stability of the triarylcyclopropenium ions with that for the triarylmethyl cations, the reported pK_{R^+} values[5,13] for the triarylcyclopropenium ions together with the present data were plotted against those[12,14] for the corresponding triarylmethyl cations. As shown in Fig. 3 there exists a reasonable linear free-energy relationship for the pK_{R^+} values between the two systems. However, the slope (0.46) is much smaller than unity, *i.e.*, the conjugative interaction of the substituent to stabilize the cationic center is apparently smaller in the triarylcyclopropenium system than in the triarylmethyl sys-

tem. This phenomenon is consistent with the results of the ^{13}C NMR measurements,[5,10] which implies that the positive charge in the triphenylcyclopropenium ion (**4**) resides mostly in the central three-membered ring to retain the "aromatic" 2π-electron ring system so that less of the charge is delocalized to the *para*-position to interact with the substituents than in the case of the triarylmethyl system, even though the coplanarity of the whole π-system is more favored in the triarylcyclopropenium system.

Experimental

General. The melting points are uncorrected. The elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto. The IR and UV spectra were recorded on Hitachi 215 and Hitachi 200-10 spectrometers, respectively. The ^1H NMR spectra were taken with a Hitachi R-24 spectrometer with tetramethylsilane as the internal standard. The ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer operated in the Fourier transform mode.

Materials. All the reagents employed were of reagent grade quality except when otherwise stated. Tetrachlorocyclopropene (C_3Cl_4) was supplied by Aldrich Chemical Co. Cyclopropylbenzene[15] and *p*-bromocyclopropylbenzene[16] were prepared according to the literature.

Bis(cyclopropylphenyl)cyclopropenones ***1a***, ***1b***, *and* ***1c***. To a stirred suspension of $C_3Cl_3^+AlCl_4^-$, prepared from C_3Cl_4 (1.12 g; 6.29 mmol) and $AlCl_3$ (0.67 g, 5.0 mmol) in dichloromethane (CH_2Cl_2 ; 2.5 ml), was added dropwise a solution of cyclopropylbenzene (1.32 g; 11.2 mmol) in CH_2Cl_2 (5 ml) at -60 °C under an atmosphere of nitrogen. When the temperature was raised slowly to -10 °C, rapid evolution of HCl took place accompanied by a sudden color change to dark red. The mixture was further stirred at 0 °C for 1 h and then hydrolyzed with cold water (10 ml). The aqueous layer was extracted with CH_2Cl_2 (5 ml × 3). The combined organic solution was washed with 10% NaCl, dried ($MgSO_4$), and evaporated *in vacuo* to give 2.016 g of the crude product, from which was separated the cyclopropenone **1a** (0.216 g) as a white powder by washing with ether (3 ml). The remaining mixture was separated by the use of preparative TLC over SiO_2 (Merck, PF_{254}) developed with benzene–ether(4 : 1). The fraction with an R_f 0.14 afforded an additional amount of **1a** (0.231 g; total yield 31.2%). Purification was effected by recrystallization from benzene. Found: C, 88.35; H, 6.25%. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.33%. The next TLC fraction with an R_f 0.34 gave the cyclopropenone **1b** (0.675 g; 47.2%) as a white powder from benzene. Found: C, 88.09; H, 6.25%. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.33%. The last fraction with an R_f 0.64 afforded the cyclopropenone **1c** (0.106 g; 7.4%) as a white powder from benzene–hexane. Found: C, 88.31; H, 6.63%. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.33%. The yields for the cyclopropenone isomers in duplicate runs were 29.8 and 23.8% for **1a**, 57.2 and 45.2% for **1b**, and 7.4 and 8.9% for **1c**.

*Tris(*p*-cyclopropylphenyl)cyclopropenium Tetrafluoroborate (***2*** BF_4^-). Method A*:[17] To a stirred solution of *p*-cyclopropylphenylmagnesium bromide, prepared from *p*-bromocyclopropylbenzene (0.592 g; 3.00 mmol) and magnesium (0.081 g; 3.3 mg atom) in dry ether (10 ml), was added a solution of the cyclopropenone **1a** (0.231 g; 0.808 mmol) in dry benzene (20 ml) during a 25-min period at 0 °C. After stirring for 1.5 h at 0 °C, the mixture was hydrolyzed with 0.2 M KH_2PO_4 (30 ml) and worked up in the usual manner. Addition of 42% aq HBF_4 (1 ml) to the stirred solution of the crude product in ether (30 ml) gave a white precipitate, which was collected, washed with ether, and vacuum-dried to give the tetrafluoroborate salt of the cation **2** as a white powder (0.006 g; 2%). Found: C, 75.88; H, 5.59%. Calcd for $C_{30}H_{27}BF_4$: C, 75.96: H, 5.74%.

Method B: A solution of the cyclopropenone **1a** (0.169 g; 0.590 mmol) and thionyl chloride (0.334 g; 2.81 mmol) in dry benzene was stirred at room temperature for 30 min and then refluxed for 15 min. Evaporation of the mixture *in vacuo* left crude 1,2-bis(*p*-cyclopropylphenyl)-3,3-dichlorocyclopropene as a brownish sludge. The dichlorocyclopropene was dissolved in dry ether (2 ml) and added to a stirred solution of *p*-cyclopropylphenylmagnesium bromide, prepared from *p*-bromocyclopropylbenzene (0.299 g ; 1.51 mmol) and magnesium (0.041 g; 1.7 mg atom) in dry ether (2 ml), at 0 °C. After stirring at 0 °C for 30 min and at room temperature for 24 h, the mixture was hydrolyzed with 0.2 M KH_2PO_4 (20 ml) and worked up. The crude product was dissolved in ether (2 ml) and treated with 1 ml of a solution of acetic anhydride–42% aq HBF_4 (10 : 1) to give the cation salt **2** BF_4^- (0.005 g; 2%).

Method C: *Synthesis of Bis(*p*-cyclopropylphenyl)cyclopropenium Tetrafluoroborate (***3*** BF_4^-).* Following the method reported by Perkins and Wadsworth[18] for the reduction of diphenylcyclopropenone, the cyclopropenone **1a** was converted to 1,2-bis(*p*-cyclopropylphenyl)cyclopropene by reaction with borane–trimethylamine complex and HCl; mp 75.5—78.0 °C; IR ν(KBr) 1825 cm^{-1} (C=C stretching in the cyclopropene ring); ^1H NMR δ ($CDCl_3$) 7.64 (d, 4H, *o*-H), 7.14 (d, 4H, *m*-H), 1.95 (m, 2H, methine), 1.50 (s, 2H, CH_2-(cyclopropene)), 1.1—0.7 (m, 8H, CH_2(cyclopropane)); ^{13}C NMR δ 144.5 (s, C-5), 129.8 (d, C-3), 127.8 (s, C-2), 126.0 (d, C-4), 110.4 (s, C-1), 15.8 (d, C-6), 9.9 (t, C-7), 6.5 (t, C-8).

Into a refluxing solution of triphenylmethyl tetrafluoroborate[19] (1.532 g; 4.64 mmol) in CH_2Cl_2 (7 ml) was added dropwise during a 1.5-h period with stirring a solution of 1,2-bis(*p*-cyclopropylphenyl)cyclopropene (0.421 g; 1.55 mmol) in CH_2Cl_2 (10 ml). The solution was further refluxed for 10 min, and then concentrated to *ca.* 8 ml. Addition of ether (50 ml) produced a yellow precipitate, which was collected and washed with ether to give the tetrafluoroborate salt of the cation **3** as a brownish yellow powder (0.336 g; 60.6%). Found: C, 70.27; H, 5.48%. Calcd for $C_{21}H_{19}BF_4$: C, 70.42; H, 5.35%.

Determination of pK_{R^+}. The pK_{R^+} value was determined in 23% aqueous ethanol at 25 °C following the spectrophotometric method described by Breslow and Chang.[13] The cationic solution was found to be stable over the whole pH range examined. The pH values were read on a Horiba model H pH meter precalibrated with standard buffers.

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