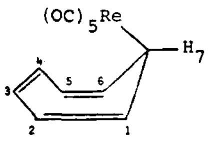
Table I. Spin Saturation Transfer Data for **2**[a]

T, *K*	T_1 of $H_{1,6}$[b]	$\frac{M_z(0) - M_z(\infty)}{M_z(\infty)}$[c]	$k \times 10^2$, s^{-1} [d]
298	6.47	0.11	1.70
301	6.87	0.19	2.77
304	7.27	0.23	3.16
307	7.67	0.38	4.95
310	8.07	0.47	5.83

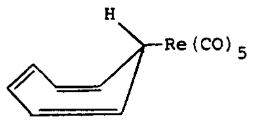
[a] In dioxane-d_8 solvent. [b] Measured using a π, τ, $\pi/2$, $5T_1$ sequence. [c] $M_z(0)$ is the normal equilibrium magnetization of $H_{1,6}$ and $M_z(\infty)$ is the equilibrium magnetization of $H_{1,6}$ with saturation of H_7. [d] The rate constant, *k*, for exchange in a two-site equal population system is given by $k = 1/T_{1(1,6)}[(M_z(0) - M_z(\infty)/M_z(\infty)]$.[23] The two-site treatment is adequate since the rate of 1,3 and 1,4 shifts is zero in the temperature range studied.

bility. The result demonstrates for the first time a clear difference between main and transition group systematics, posing an interesting problem for the theory of sigmatropic shifts.

Two conformations are possible for **2**, which may have the $Re(CO)_5$ moiety in a quasi-axial (**2a**) or quasi-equatorial (**2b**) position. The observed H_1–H_7 coupling constant in **2** is 8.7 Hz, similar to the value of 8 Hz observed for the triphenyltin derivative **3**;[20] **3** has been shown by X-ray crystallography to have the substituent in the quasi-axial position.[22] If it is the case that **2a** is the predominant or only conformer present in solutions of **2**, there should be no geometric constraint on a 1,5 shift, and the different migration pathways of the rhenium and tin compounds must be otherwise explained.



2a



2b

We are continuing this investigation on the assumption that other stable *monohapto*-7-cycloheptatrienyl derivatives of transition metals can be synthesized and that their study will contribute to the understanding of fluxional processes in organometallic chemistry.

Acknowledgment. We thank the National Research Council for financial support and for a grant that made possible the acquisition of the 400-MHz NMR instrument. We also thank T. Nakashima, G. Bigham, and T. Brisbane for invaluable assistance and advice on NMR problems.

References and Notes

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(4) M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 2021 (1956).

(5) Compound **1** was isolated in 70% yield as pale yellow crystals: mp 98 °C; IR (cyclohexane, ν_{CO} with assignment, cm^{-1}) 2132 (w, A_1), 2061 (w, B_1), 2023 (s, E), 2014 (s, E), 1999 (s, A_1), 1637, 1626 (w, acyl CO); ^1H NMR (methylcyclohexane-d_{14}, δ) 6.51 (m, $H_{3,4}$), 6.18 (m, $H_{2,5}$), 5.12 (m, $H_{1,6}$), 2.50 (t, H_7) ($^3J_{17}$ = 5.8 Hz). Anal. Calcd for $C_{13}H_7O_6Re$: C, 35.04; H, 1.57. Found: C, 35.08; H, 1.70.

(6) Hanovia 140-W lamp, quartz vessel, acetone, −78 °C.

(7) The yield of **2** in decarbonylation step was 60%: mp 74 °C; IR (cyclohexane, ν_{CO}, cm^{-1}) 2120 (w), 2015 (s), 1983 (m); mass spectrum, molecular ion of correct isotope pattern at *m/e* 418; ^{13}C NMR (0 °C, methylcyclohexane-d_{14}, 22.6 MHz, δ) 17.71 (C_7), 122.09 ($C_{2,5}$), 135.73 ($C_{3,4}$), 140.14 ($C_{1,6}$), 181.1 (axial ReCO), 187.0 (equatorial ReCO) (olefinic ^{13}C assignments by selective proton decoupling); ^1H NMR (30 °C, methylcyclohexane-d_{14}, 400 MHz, δ) 3.16 (tt, H_7), 5.24 (m, $H_{2,5}$), 5.44 (m, $H_{1,6}$), 5.96 (m, $H_{3,4}$) ($^3J_{17}$ = 8.7, $^4J_{27}$ = 1.0, $^3J_{12}$ = 10.1 Hz). Anal. Calcd for $C_{12}H_7O_5Re$: C, 34.52; H, 1.69. Found: C, 34.54; H, 1.78.

(8) The manganese analogue of **1** is known, but only (η^5-C_7H_7)$Mn(CO)_3$ was isolated after low temperature irradiation.[9]

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(13) For a readable account of this method, cf. J. W. Faller in "Determination of Organic Structures by Physical Methods", Vol. 5, F. C. Nachod and J. J. Zuckerman, Eds., Academic Press, New York, 1973, Chapter 2.

(14) Dioxane was used in the quantitative experiments because the stability of **2** was somewhat greater in this solvent than in methylcyclohexane. Qualitative conclusions from spin saturation transfer experiments are the same in both solvents. Some line broadening was observed at 70 °C in methylcyclohexane, but the migration pathway could not be studied by this method as decomposition was too rapid at this temperature.

(15) Saturation of H_7 at 15 °C results in no nuclear Overhauser enhancement of the $H_{1,6}$ signal.

(16) The same conclusion was reached from ^{13}C NMR studies, in which irradiation at δ 17.71 diminished the peak at 140.14 but not the others. Quantitative treatment of the ^{13}C data is complicated by the widely different relaxation times of C_7 (1.4 s) and $C_{1,6}$ (2.7 s).

(17) The error limits quoted are standard deviations of the least-squares straight line in the Eyring plot and consequently give only minimum errors.

(18) This small negative entropy of activation is not consistent with a dissociative process. Preliminary studies of the kinetics of thermal decomposition of **2** (in which cycloheptatriene, ditropyl, and $Re_2(CO)_{10}$ are formed) in dioxane led to $\Delta G^{\ddagger} \simeq$ 25 kcal mol^{-1} at 42 °C. This value must represent a minimum activation energy for homolysis to $\cdot Re(CO)_5$ and $\cdot C_7H_7$ fragments; so we conclude that such bond breaking is not significant in the observed migration.

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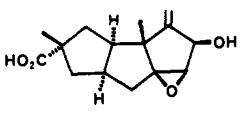
A New, Stereocontrolled Synthesis of *cis,anti,cis*-Tricyclo[6.3.0.0^{2,6}]undecanes. Total Synthesis of (±)-Hirsutene

Sir:

The *cis,anti,cis*-tricyclo[6.3.0.0^{2,6}]undecane system is found in the carbon skeleton of the hirsutane group of sesquiterpenes, as for example, hirsutic acid[1] (**1**), coriolin[2] (**2**), and their biogenetic precursor, hirsutene[3] (**3**). These substances are known to be endowed with remarkable biological properties and have been the subject of intense synthetic investigation, recently culminating in the description of the biogenetic-like synthesis of hirsutene[4] and a stereocontrolled synthesis of hirsutic acid.[5]



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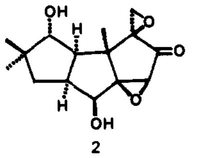

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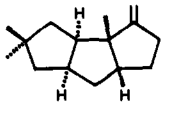
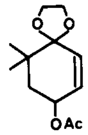


3

We report herein a new stereocontrolled synthesis of hirsutene and the chemical precursors of coriolin and thus record a general method of entry into the *cis,anti,cis*-tricyclo[6.3.0.0^{2,6}]undecane series. The key step in this approach is a unique skeletal rearrangement of a tricyclic 6-4-5-fused ring to a cis,anti,cis-tricyclic 5-5-5-fused ring. The cis,syn,-cis-tricyclic series, the stereochemistry of which is incompatible with that of the hirsutane skeleton, have been synthesized by photocycloaddition.[6]

0002-7863/79/1501-6116$01.00/0

Our synthesis begins with the preparation of the starting ethylene ketal (4,[7] bp ~57 °C (0.005 mm)) from 2,2-dimethylcyclohexanone in 54% overall yield in five steps: (1) bromine/THF, 10 °C; (2) ethylene glycol/TsOH/benzene, reflux; (3) potassium *tert*-butoxide/Me$_2$SO, 15 °C; (4) *N*-bromosuccinimide/benzoyl peroxide/CCl$_4$, reflux; (5) AcOAg/ether, 20 °C. The photocycloaddition of a simple cyclohexenone derivative to cyclopentane-1,3-dione enol acetate has been developed by de Mayo et al.,[8] and modified by others,[9] giving the tricyclic 6-4-5-fused ring. Irradiation of a solution of the ketal **4** (21.0 g) and 2-methylcyclopentane-1,3-dione enol acetate (**5**,[8] 1.73 g) in cyclohexane (31 mL), through a Pyrex filter using a high-pressure 400-W mercury lamp, for 60 h at 20 °C under argon gave two adducts of structures **6**[7] (mp 213-214 °C, 35% yield from **5**) and **7**[7] (mp 193-196 °C, 1% yield from **5**), with recovery of the starting ketal **4** (18.9 g) after silica gel column chromatography (on silica gel TLC, hexane-EtOAc, 2:1; R_f 0.63, 0.32, 0.28, and 0.24 for **4**, **5**, **6**, and **7**). Their structures were determined to be the cis,anti,trans, head-to-head forms by X-ray crystallographic analysis[10] of the *p*-bromobenzoates **10**[7] (Figure 1, mp 169 °C) and **11**[7] (mp 199 °C) of the corresponding alcohols **8**[7] and **9**,[7] which were in turn prepared from **6** and **7** by sodium borohydride reduction in methanol. The adduct **7** apparently resulted from an allylic migration of the acetoxy group of ketal **4** before its cycloaddition to **5**. It was noteworthy that no other stereoisomers could be isolated in significant yields. Also, **6** possesses a highly twisted trans 4-6-fused ring, which was expected to provide the driving force for the forthcoming rearrangement.



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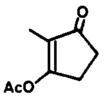

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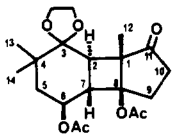

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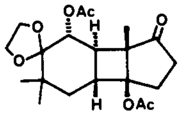

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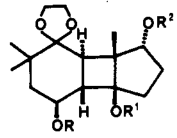
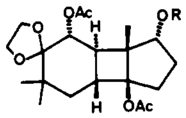


8: R=R^1=Ac, R^2=H

10: R=R^1=Ac, R^2=COC$_6$H$_4$Br

12: R=R^1=H, R^2=CH$_2$OCH$_3$

13: R=Ts, R^1=H, R^2=CH$_2$OCH$_3$



9: R=H

11: R=COC$_6$H$_4$Br

Protection of **8** with a methoxymethyl group (methoxymethyl chloride and *N*,*N*-diisopropylethylamine, 20 °C, 5 h), followed by removal (sodium methoxide, 20 °C, 24 h) of the acetyl group, gave the diol **12**[7] (foam, overall yield 74%) which, in turn, when treated with 4 equiv of *p*-toluenesulfonyl chloride in pyridine at 19 °C for 4 h, yielded the labile monotosylate **13**[7] (mp 105-106 °C, yield 82%) after Sephadex LH-20 column chromatography (on silica gel TLC, hexane-methyl ethyl ketone, 2:1; R_f 0.02 and 0.38 for **12** and **13**). In the NMR spectrum, the H-6 signal showed a double triplet ($J_{5,6} = J_{6,7} = 10$, $J_{5',6} = 5.5$ Hz), which was similar to those of **8** and **10**, suggesting that the six-membered ring in **13** existed in a chair form with an equatorial tosyloxy group. Conformationally, **13** is considered to adopt a similar form to that of **10** (Figure 1), and the migrating C-2–C-7 bond can be trans coplanar to the C-6–tosyloxy bond, while the C-7–C-8 bond can not be coplanar. Therefore, the sequential skeletal rearrangement of **13** is facilitated by the breaking of parallel bonds to give, stereospecifically, the desired tricyclic 5-5-5-fused ring, *cis,anti,cis*-tricyclo[6.3.0.0^{2,6}]undecane derivative and not the undesired 6-5-5-fused ring, tricyclo[5.3.1.0^{2,6}]undecane derivative.[11]

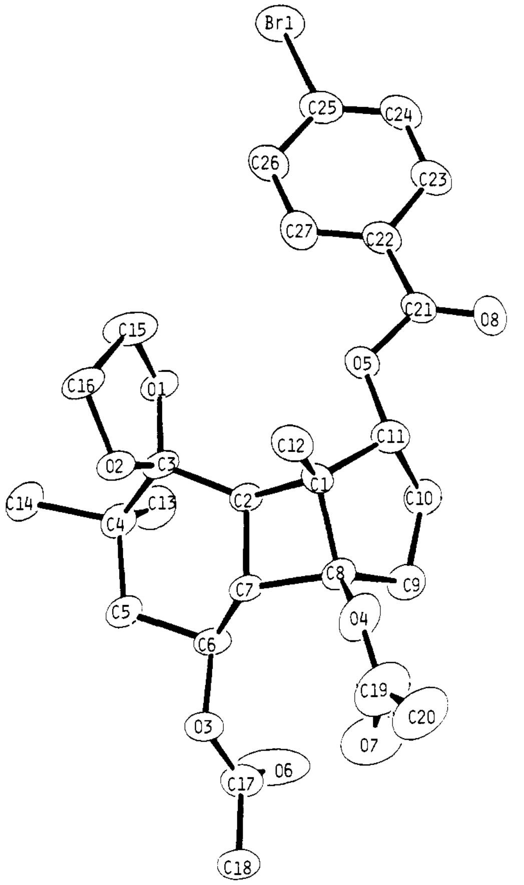
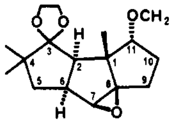
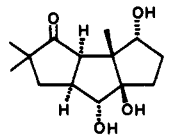


Figure 1. A structural view of **10** as seen by X-ray analysis. The final *R* factor was 0.112 for 2857 planes measured by Cu Kα radiation.

When treated with 1 equiv of potassium carbonate in 60% aqueous acetone in a sealed tube at 85 °C for 1 day, **13** furnished a single product **14**[7] (oil, yield 90%). The IR spectrum of **14** showed an absence of hydroxyl groups, and the molecular weight (M$^+$ 324) and elemental analysis showed the chemical formula to be $C_{18}H_{28}O_5$, suggesting that **14** was the β-epoxide, which could be reasonably formed by an adjacent attack of the C-8 hydroxyl oxygen on an intermediary carbonium ion at C-7. The cis,anti,cis stereochemistry was confirmed by direct-method X-ray analysis[10] of the corresponding ketotriol **15**[7,12] (mp 172 °C), prepared from **14** by treatment with 1% sulfuric acid in aqueous acetone (45 °C, 3 days, yield 81%), demonstrating that **14** and **15** could be suitably functionalized intermediates for the synthesis of coriolin-related compounds.

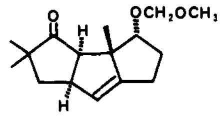


14



15

The stage was thus set for the synthesis of (±)-hirsutene (**3**). Treatment of **14** with 10 equiv of sodium iodide and 10 equiv of zinc in 97% aqueous DMF at 130 °C for 2 days, followed by deketalization with 0.1% sulfuric acid in aqueous acetone at 20 °C for 4 h, gave the unsaturated ketone **16**[7] (oil, overall yield 56%). Highly stereoselective reduction of **16** over Pd black in MeOH under 3 atm of hydrogen, followed by treatment with LiAlH$_4$ in THF, afforded as a single product the



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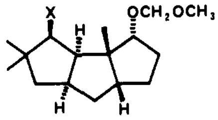
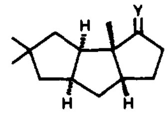


17 : X = OH

18 : X = OCS_2CH_3

19 : X = H



20 : Y = $<^{OH}_{H}$

21 : Y = O

tricyclic alcohol **17**[7] (oil, overall yield 87%). Assignment of the stereochemistry at C-3 and C-8 in **17** was based on a presumed attack by the reagents from the less hindered sides, and on the difficulty in forming a trans 5-5-fused ring,[13] in addition to the NMR spectrum. Deoxygenation of **17** using Barton's procedure,[14] which consisted of tri-*n*-butyltin hydride reduction of the corresponding *S*-methyl dithiocarbonate **18**,[7] gave the product **19**[7] (oil, yield 90%), which was deprotected (1% H_2SO_4 in aqueous acetone, 50 °C) to give the alcohol **20**[7] (oil) quantitatively. Oxidation of **20** with pyridinium chlorochromate in methylene chloride then gave the nor ketone **21**[7] (mp 44-45 °C, yield 86%). The spectral data (IR, NMR, and mass) were completely identical with those of an authentic sample[15] obtained from natural hirsutene. Since the nor ketone has been transformed into hirsutene,[3] the synthesis of **21** constitutes the completion of the task. Now that the utility of this unique skeletal rearrangement for a stereocontrolled synthesis of the hirsutane skeleton has been illustrated, the synthesis of highly oxidized coriolin-related substances is the subject of current studies.

Acknowledgment. We are grateful to Professor Sumio Umezawa, Director of the Institute of Bioorganic Chemistry, and Professor Hamao Umezawa, Director of the Institute of Microbial Chemistry, for their generous support of our program. We also are indebted to Professor Yoichi Iitaka,[10] Ms. Hikaru Nakamura,[10] and Professor Shigeo Nozoe.[15]

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(7) All compounds gave satisfactory combustion analyses, IR, NMR and mass spectra consistent with the reported structures. Melting points were uncorrected. Unless otherwise noted, NMR (δ, parts per million from Me_4Si) spectra were in $CDCl_3$ solution. Significant NMR spectral data are listed herein. **4**: 1.02, 1.08 (each s, Me), 2.08 (s, OAc). **6**: 0.87, 1.09, 1.16 (each s, Me), 2.01, 2.06 (each s, OAc), 5.01 (dt, $J_{5,6} = J_{6,7} = 10$, $J_{5',6} = 6$ Hz, H-6). 7: 0.91, 1.09, 1.24 (each s, Me), 2.01, 2.03 (each s, OAc), 5.25 (d, $J_{2,3} = 11$ Hz, H-3). **8**: 0.87, 1.15, 1.24 (each s, Me), 1.96, 2.03 (each s, OAc), 5.16 (dt, $J_{5,6} = J_{6,7} = 10$, $J_{5',6} = 6$ Hz, H-6). **10**: 0.88, 1.16, 1.26 (each s, Me), 1.99, 2.04 (each s, OAc), 5.15 (dt, $J_{5,6} = J_{6,7} = 10$, $J_{5',6} = 6$ Hz, H-6), 5.3 (m, H-11). **11**: 0.91, 1.12, 1.25 (each s, Me), 1.67, 2.03 (each s, OAc). **13**: 0.83, 1.07, 1.23 (each s, Me), 2.01 (d, $J_{2,7} = 14$ Hz, H-2), 2.44 (s, Me of Ts), 2.60 (dd, $J_{6,7} = 10$ Hz, H-7), 4.68 (dt, $J_{5,6} = 10$, $J_{5',6} = 5.5$ Hz, H-6). **14**: 0.96, 0.99, 1.10 (each s, Me), 1.44, 1.76 (each dd, $J_{5,5'} = 12.5$, $J_{5,6} = J_{5',6} = 9$ Hz, H-5 and -5′), 2.66 (ddt, $J_{2,6} = 11.5$, $J_{6,7} = 2.5$ Hz, H-6), 3.10 (d, H-2), 3.19 (d, H-7), 3.61 (d, $J_{10,11} = 5$, $J_{10',11} = 0$ Hz, H-11). **17**: 0.97, 1.05, 1.18 (each s, Me), 3.58 (dd, $J_{2,3} = 9$, $J_{3,OH} = 3.5$ Hz, H-3, which, on adding 1 drop of D_2O, collapsed to a doublet), 3.82 (dd, $J_{10,11} = 7.5$, $J_{10',11} = 5$ Hz, H-11). **20**: 0.96, 0.98, 1.07 (each s, Me), 3.80 (m, H-11). **21** (CCl_4): 0.89, 0.94, 1.05 (each s, Me).

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(10) The X-ray crystallographic analysis was kindly carried out by Professor Yoichi Iitaka and Ms. Hikaru Nakamura, Faculty of Pharmaceutical Sciences, University of Tokyo. Details of the analysis will be published in *Bull. Chem. Soc. Jpn.*

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(12) The IR spectrum showed the low-frequency shift of the carbonyl absorption (1715 cm^{-1}), supporting the strong hydrogen bonding between the C-3 carbonyl group and the C-11 hydroxyl group. This fact was also confirmed by the X-ray analysis.

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(15) The IR, NMR, and mass spectra of the naturally derived nor ketone were provided by Professor Shigeo Nozoe, Tohoku University, Pharmaceutical Institute.

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A Nuclear Magnetic Resonance Study of the Bis(2,2′-bipyridine)platinum(II) Cation in Basic Solution

Sir:

The reactions of nucleophiles with metal complexes containing phen and bpy[1] have recently collectively been attributed to attack on the ligand so that the chemistry of this important and large group of complexes has been relegated to what is essentially claimed to be the organic chemistry of the ligands.[2] For certain specific reactions involving octahedral complexes, this may be so, For four-coordinate complexes of Pt(II) and Pd(II) it has been challenged.[3]

The title complex (which because of steric hindrance is not strictly planar[3]) is known to react with base according to

$$[Pt(bpy)_2]^{2+} + OH^- \overset{K}{\rightleftarrows} [Pt(bpy)_2OH]^+ \qquad (1)$$

$$[Pt(bpy)_2OH]^+ + H_2O \xrightarrow{k} [Pt(bpy)(OH)(OH_2)]^+ + bpy \qquad (2)$$

$K = 10^{4.8}$ M^{-1} at 25 °C[3,4] so that a small excess of base gives a solution containing effectively only $[Pt(bpy)_2OH]^+$ which is long lived at room temperature; $t_{1/2} = 480$ h at 25 °C.[3] Gillard et al.[4] have presented ^1H NMR data for $[Pt(bpy)_2OH]^+$ in which new features at high field not present in $[Pt(bpy)_2]^{2+}$ were interpreted as demonstrating "nucleophilic attack (by OH^-) at the carbon atom adjacent to the ring nitrogen".[4] The quality of all of the spectra given by these authors[2] leaves much to be desired and we find their use for detailed interpretation unconvincing. We have therefore reinvestigated the ^1H NMR spectra and have also measured the corresponding ^{13}C NMR spectra.

Beer's law is obeyed for $[Pt(bpy)_2OH]^+$ over the whole concentration range and for all of the wavelengths investigated (1×10^{-6} to 4×10^{-2} M, 240-480 nm). The spectra were independent of anion, ClO_4^- or NO_3^-, and there were no absorption bands in the visible or the near-infrared region up to 1200 nm. We conclude therefore that polymerization is negligible.

From potentiometric titrations of $[Pt(bpy)_2]^{2+}$ with base we find that only *one* (1.02 ± 0.03) OH^- is present in $[Pt(bpy)_2OH]^+$. ^{13}C and ^1H NMR spectra (for system of numbering, see Figure 1) in neutral solution are given in Figures 2 and 3. Both spectra show that all four aromatic rings are

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