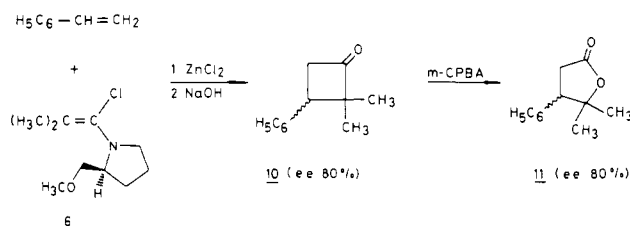Scheme IV

have been revealed as demonstrated by the spectrum of racemic **9** in the presence of Eu(hfc)$_3$.

The structure and configuration of the adduct was established by an X-ray diffraction analysis of **8**, recrystallized (CHCl$_3$–Et$_2$O) as a perchlorate.[7] The absolute configuration of **8** followed from the known chirality of the inductor, and the configuration at the ring fusion was found to be (1*R*,5*S*). Thus, in addition to providing a much higher enantiomeric excess (>97% vs. 55.4%), the reaction of cyclopentene with the β-disubstituted ketene iminium salt **5** also produces an adduct that is of *opposite configuration*[8] to that formed from the unsubstituted keteneiminium salt **2**.

These differences are readily understood when one considers steric interactions in the two possible perpendicular approaches (Scheme III).[9] Transition state A leads to the 1*S*,5*S* configuration in the adduct and is favored when R = H. When the β-hydrogen substituents of the ketene iminium salt are replaced by bulkier groups (R = CH$_3$), transition state A becomes highly hindered. The product results exclusively from transition state B and has then 1*R*,5*S* configuration at the ring junction. Moreover, from the absolute configuration of **8** it could be inferred that in transition state B the methoxymethyl group was directed toward the olefin. This suggests a stabilizing interaction between the oxygen lone pair and the developing positive charge on the olefinic carbon atoms.[10]

Although the mechanistic discussion presented here can only be considered tentative, the examples represent useful models for designing chiral partners for [2 + 2] cycloaddition reactions with olefins.[11] Preliminary studies on the reaction of **5** with acyclic olefins were quite promising (Scheme IV). Thus, cycloaddition of **5** (**6** + ZnCl$_2$) to styrene gave, after hydrolysis (0.1 N NaOH), cyclobutanone **10** [55% from **7**, bulb-to-bulb 125 °C (0.1 torr,

(7) The structure was solved by MULTAN 80 (Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J. P. "MULTAN 80: A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; York, England, Louvain-La-Neuve, Belgium, 1980) and refined by the SHELX 76 program (Sheldrick, G. M. "SHELX 76: Program for Crystal Structure Determination"; University of Cambridge, England, 1976) on the basis of 1111 observed reflections for which $I > 2.5\sigma$ (*I*). Incident radiation was Mo Kα ($\lambda = 0.71069$ Å). The final *R* value is 0.070. Crystal data: C$_{15}$H$_{26}$O$_5$ClN: orthorhombic space group $P2_12_12_1$; cell dimensions $a = 7.178$ (2), $b = 14.035$ (4), $c = 17.331$ (6) Å; $V = 1746.0$ (9) Å^3; $Z = 4$. Coordinates and molecular dimensions are available from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

(8) From the sequencing rule it follows that bicyclo[3.2.0]heptan-6-ones **3a** and **9** of the same absolute configuration are described as 1*R*,5*R* for the 7-unsubstituted compound **3a** and 1*R*,5*S* for the 7-dimethyl derivative **9**.

(9) Ghosez, L.; O'Donnell, M. J. In "Pericyclic Reactions", Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 2, pp 79.

(10) (a) Meyers, A. I. *Acc. Chem. Res.* **1978**, *11*, 375. (b) Enders, D.; Eichenauer, H. *Chem. Ber.* **1979**, *112*, 2933. (c) Mukaiyama, T.; Soai, K.; Sato, T.; Shimizu, H.; Suzuki, K. *J. Am. Chem. Soc.* **1979**, *101*, 1455. (d) Kolb, M.; Barth, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 725.

(11) For earlier examples of asymmetric [2 + 2] cycloadditions to olefinic double bonds, (a) Sulfene + enamines: Paquette L. A.; Freeman, J. P.; Maiorama, S. *Tetrahedron* **1971**, *27*, 2599. (b) Allene + acrylonitrile: Baldwin, J. E.; Roy, U. V. *J. Chem. Soc., Chem. Commun.* **1969**, 1225. Baldwin, J. E.; Fleming, R. H. *Fortschr. Chem. Fortsch.* **1970**, *15*, 281. (c) Allene + ketenes: Bertrand, M.; Le Gras, J.; Goré, J. *Tetrahedron Lett.* **1972**, 2499; Ducan, W. G.; Weyler, W., Jr.; Moore, H. W. *Tetrahedron Lett.* **1973**, 4391. Bampfield, H. A.; Brook, P. R. *J. Chem. Soc., Chem. Commun.* **1974**, 171. Bamfield, H. A.; Brook, P. R.; Mc Donald, W. S. *Ibid.* **1975**, 132. (d) Allene dimerizations: Moore, W. R.; Bach, R. D.; Ozretich, T. M. *J. Am. Chem. Soc.* **1969**, *91*, 5918. (e) Olefin dimerizations: Elgavi, A.; Green, B. S.; Schmidt, G. M. J. *Ibid.* **1973**, *95*, 2058. Green, B. S.; Rabinsohn, Y.; Rejtö, M. *J. Chem. Soc., Chem. Commun.* **1975**, 313. Green B. S.; Hagler, A. T.; Rabinsohn, Y.; Rejtö, M. *Isr. J. Chem.* **1976/1977**, *15*, 124.

[α]^{25}$_D$ −33.6°, *c* 2.3, CHCl$_3$, ee = 80% by NMR, 200 MHz, CDCl$_3$ + (Eu(hfc)$_3$)]. Bayer–Villiger oxidation (*m*-CPBA, NaHCO$_3$) of **10**, provided a quantitative yield of the chiral lactone **11** ([α]$_D$^{20} −63.03°, *c* 3.3, CH$_2$Cl$_2$, ee = 80%).

Work is now in progress to develop reagents for the asymmetric alkylation of olefins and for the enantioselective synthesis of β-lactams by [2 + 2] cycloadditions to imines.

Supplementary Material Available: Crystallographic data for compound **8** (2 pages). Ordering information is given on any current masthead page.

Intersystem Crossing in Styrene and Styrene Derivatives

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We report experimental results disproving the common idea that the quantum yield of intersystem crossing is extremely low for styrene and styrene derivatives. This assumption, which appears in nearly every paper dealing with photophysics of styrenes,[1] is founded on the inefficiency of large-size phenylcycloalkenes to sensitize the phosphorescence of biacetyl.[2] It was reinforced by the failure of several attempts to observe the phosphorescence of styrenic compounds.[3,4] It is now obvious that the method of the sensitized phosphorescence of biacetyl is totally unsuitable for measuring ϕ_{is} in 1-phenylcyclohexene (PC6) and other large-size phenylcycloalkenes since the only metastable triplet of these compounds is a perpendicular triplet nearly degenerate in energy with the ground state of the same geometry[5] and thus unable to sensitize the biacetyl triplet.

Observation by laser-flash photolysis of a triplet–triplet (T–T) absorption of styrenic compounds allowed us to measure ϕ_{is} by the following sequence: (a) measurements of the T–T absorption following direct excitation, (b) evaluation of the number of excited molecules from the amount of excitation energy absorbed, and (c) determination of the extinction coefficient for the T–T transition.

Styrenes, in argon-flushed cyclohexane, were excited at 249 nm by an excimer laser pulse (Lambda-Physik EMG 500, KrF, pulse characteristics: 30–100 mJ, 15–20 ns). The transient T–T absorption was measured at 325 nm, using a crossed-beam arrangement and an He–Cd laser (Liconix 4050–UV) as monitoring light source. Thus the detection system (monochromator and photomultiplier) could be placed several meters away from the sample cell in order to suppress the effects of the strong fluorescence emitted by the solution.

The decay times of the transient absorptions observed under these conditions for a number of styrenes are identical, within experimental uncertainty, with lifetimes measured by triplet

(1) See for instance ref 3b, 4, 5a, and 10.
(2) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718–3725.
(3) (a) Crosby, P. M.; Dyke, J. M.; Metcalfe, J.; Rest, A. J.; Salisbury, K.; Sodeau, J. R. *J. Chem. Soc., Perkin, Trans 2* **1977**, 182–185. (b) Lyons, A. L.; Turro, N. J. *J. Am. Chem. Soc.* **1978**, *100*, 3177–3181.
(4) Condirston, D. A.; Laposa, J. D. *Chem. Phys. Lett.* **1979**, *63*, 313–317.
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Table I

compd	$OD_{(tr)}$	E_{mJ}	$\phi_{isc}\epsilon$	ϵ_{325}	$\phi_{isc}{}^{a}$	τ_f, ns	$10^7 k_{isc}$, s	$^3\tau$, ns
PhCH=CH$_2$	0.27	30	865	2200	0.395	13.9[b]	2.85	≃25
PhCH=CH(C$_2$H$_5$)	0.17	37	444	3500	0.127	4.3	2.9	≃30
PhC(CH$_3$)=CH(C$_2$H$_5$)	0.07	39	172	4000	0.043	1.8	2.4	≃38
PC6	0.08	39	196	4400	0.044	1.6[c]	2.75	≃65
PN	0.77	30	2468	17900	0.138	3.7	3.7	≥2000

[a] Owing to the number of steps involved in the determination of ϕ_{isc}, the uncertainty in the ϕ_{isc} values is estimated to 15–20%. [b] From ref 4. [c] Mean value of the lifetimes given in ref 2 and 10.

sensitization,[5] indicating that these transient absorptions originate from the triplet state. Since the duration of the excitation laser pulse and the lifetimes of the excited singlets (τ_f) are not much shorter than the triplet lifetimes ($^3\tau$), the maximum values of the transient absorptions were multiplied by a correction factor that accounts for the decay of the triplet species during the excitation and intersystem-crossing processes. The factor was determined as follows. The population of the triplet state was calculated by a computer integration of the differential equations

$$d[S^*]/dt = I_t - k_1[S^*] \qquad d[T]/dt = k_{is}[S^*] - k_3[T]$$

with I_t being the intensity of the excitation as a function of time, $k_1 = 1/\tau_f$, and $k_3 = 1/^3\tau$. Thus one gets a simulation of the observed triplet concentration, whose maximum is denoted $[T]_1$. The same integration is then performed with $k_3 = 0$, giving the triplet concentration $[T]_2$ that would be obtained if the triplet state were stable. The correction factor, equal to $[T]_2/[T]_1$, does not depend on the absolute values of I_t and k_{is} and is a function of three easily measurable factors only: τ_f, $^3\tau$, and the intensity profile of the excitation pulse. The resulting corrected values of the transient absorptions, OD_{tr}, are given in Table I along with the energy of the excitation laser pulse, E_{mJ}. With S^* being the population of the excited singlet produced by the absorption of a fraction α of the incident excitation energy, E_{mJ}, in a volume V and with l being the path length of the analytical beam in the excited volume, we have

$$OD_{(tr)} = \phi_{is}S^*\epsilon l \qquad S^* = \alpha E_{mJ}K/V$$

with $K = 2.08 \times 10^{-9}$ einstein/mJ at 249 nm. From the initial absorbance of the solutions (0.15/mm), 50% of the excitation energy is absorbed in the first 2 mm of the solution through which the analytical beam is passing. But α must be somewhat lower than 0.5 since there is some depopulation of the ground state and a fraction of the laser energy may be absorbed by the triplet state. The value of α was measured by the following method: two degassed solutions in cyclohexane with the same initial absorbance at 265 nm, one containing naphthalene (NA) and the other 2-phenyl-2-norbornene (PN), were excited by 3-ns pulses at 265 nm (4th harmonic of a Nd laser), and the intensities of the T–T absorptions, $OD_{(tr)}$, were measured at 413 and 325 nm, respectively. We have

$$OD_{(tr)}{}^{NA}/OD_{(tr)}{}^{PN} = (\phi_{is}\epsilon_{413})^{NA}/(\phi_{is}\epsilon_{325})^{PN}$$

and with $\phi_{is} = 0.81$ and $\epsilon_{413} = 24000$ for naphthalene,[6,7] this gives $\phi_{is}\epsilon_{325} = 2360$ for PN. From this value and those of $OD_{(tr)}$ and E_{mJ} given in Table I for PN and with $l = 5$ cm and $V = 0.4$ cm^3, one gets $\alpha = 0.4_2$. Values of $\phi_{is}\epsilon$, calculated for the other compounds from $OD_{(tr)}$ and E_{mJ} with $\alpha = 0.4$, are given in Table I.

Extinction coefficients for the T–T absorption at 325 nm were determined by measuring, at 413 and 325 nm, the absorption of the triplet state of naphthalene and styrenes produced by sensitization by thioxanthone excited by the 3rd harmonic of the Nd laser (353 nm, 3-ns pulses). In these experiments the concentrations of naphthalene and styrenes were large enough to ensure that energy transfer always proceeds with a yield very close to unity. Under these conditions the transient absorptions are

proportional to the ϵ value and, with $\epsilon_{413} = 24000$ for naphthalene, one gest the ϵ_{325} values listed in Table I. As the number of alkyl substituents on the styrenic double bond increases, the ϵ value increases as a consequence of the hyperchromic and bathochromic effects of the alkyl group (λ_{max} for the T–T absorption of styrene is probably shorter than 325 nm) and the factor of 4 difference between ϵ_{325} for PN and PC6 may be explained by the fact that, in the triplet state, the double bond is twisted by 90° in PC6 but it cannot be twisted by a large angle in PN, so that the nature of the T–T transition is not exactly the same in both cases.

Values of ϕ_{is} calculated from ϵ and $\phi_{is}\epsilon$ are given in Table I, along with fluorescence lifetimes, τ_f, taken from the literature or measured by single-photon counting when not available. With the assumption that the triplet state is populated only (or almost exclusively) from the planar excited singlet, i.e., that intersystem crossing between the perpendicular excited singlet and triplet states is very inefficient,[8] values of the rate constant for intersystem crossing, k_{is}, are then calculated by $k_{is} = \phi_{is}/\tau_f$.

The high value of ϕ_{is} for styrene measured in this work at room temperature agrees quite well with the value that can be deduced from the lifetimes and quantum yields of fluorescence measured at 298 and 77 K in 3-methylpentane by Condirston and Laposa.[4] At 77 K and after n^2 correction for changes in the refractive index, $\phi_f = 0.34$ and $\tau_f = 18.8$ ns so that $k_f = 1.8 \times 10^7$ s^{-1} and $k_{nr} = 3.5 \times 10^7$ s^{-1}. Nonradiative processes (k_{nr}) are internal conversion (k_{ic}), twisting of the double bond (k_{tw}), and intersystem crossing (k_{is}). Twisting of the double bond must overcome an activation-energy barrier (ΔE) equal to several kcal/mol: this is shown by theoretical calculations[9,10] and by experimental facts such as the long fluorescence lifetime at 298 K (14.6 ns) and the temperature dependence of ϕ_f and τ_f. Thus at 77 K, k_{tw} must be very small and $k_{nr} \simeq k_{ic} + k_{is}$. Assuming that k_{ic} is small—comparable to k_{ic} for toluene for instance—one gets $k_{is} = 3$–3.4×10^7 s^{-1} at 77 K. If k_{is} is not strongly temperature dependent, then $\phi_{is} = 0.44$–0.50 at room temperature.

Similar value of k_{is} can be obtained from the lifetimes and quantum yields of fluorescence of several styrenes measured in the gas phase at low pressure and under excitation in the S_1, $v = 0$ state. In these conditions, k_{nr} was estimated to be 3.2×10^7, 3.3×10^7, and 3.7×10^7 s^{-1} for styrene, 1-phenylcyclobutene, and 1-phenylcyclohexene, respectively,[12] and 3.6×10^7 s^{-1} for trans-1-phenylpropene.[13] Here again twisting of the double bond cannot occur since the excited molecules are isolated and cannot gain from collisions the energy necessary to overcome the energy barrier ΔE, so that $k_{nr} = k_{is} + k_{ic}$ and, if k_{ic} is small, $k_{is} = 3$–3.5×10^7 s^{-1}.

It is clear that the results obtained by different methods converge to indicate a value of k_{is} around 3×10^7 s^{-1} for styrene and several alkyl-substituted styrenes. This is a quite unexceptional

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(9) Bruni, M. C.; Momicchioli, F.; Baraldi, J.; Langlet, J. Chem. Phys. Lett. 1975, 36, 484–488.
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(11) Crosby, P. M.; Salisbury, K. J. Chem. Soc., Chem. Commun. 1975, 477–478.
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(13) Ghiggino, K. P.; Hara, K.; Salisbury, K.; Phillips, D. J. Chem. Soc., Faraday Trans. 2 1978, 20, 607–610.

value for an aromatic hydrocarbon and is close to that reported[14] for *trans*-stilbene, 3.9×10^7 s^{-1}. An approximate value of ϕ_{is} at various temperatures or for other alkyl-substituted styrenes can probably be obtained by using the value $k_{is} = 3 \times 10^7$ s^{-1} and the fluorescence lifetime of the compound considered at the temperature of interest.

Registry No. PhCH=CH$_2$, 100-42-5; PhCH=CH(C$_2$H$_5$), 824-90-8; PhC(CH$_3$)=CH(C$_2$H$_5$), 53172-84-2; PC6, 771-98-2; PN, 4237-08-5.

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Preparation and Reactions of 1-(Phenylthio)-2-[(trimethylsilyl)oxy]-1,3-butadienes. A One-Pot Synthesis of Sulfur-Substituted 7-Hydroxybicyclo[2.2.1]heptanones: Coupling of the Diels–Alder Reaction with the Aldol Process

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In the midst of our studies directed toward the total synthesis of the rubradirins,[2] we had the occasion to prepare and to examine the properties of the new diene **1a**. This compound was produced
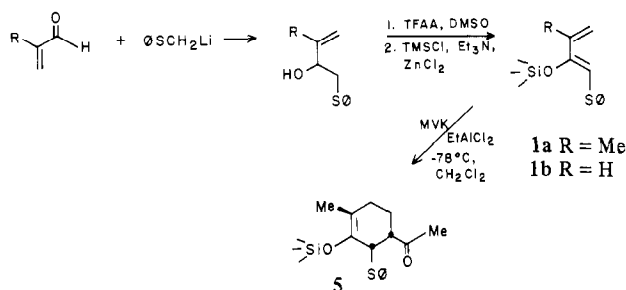
in acceptable overall yield from the alcohol formed on addition of lithiated thioanisole to methacrolein.[3] The oxidation state of this alcohol was taken to the ketone level by use of the Swern procedure, and the resulting 3-methyl-1-(phenylthio)-3-buten-2-one was trimethylsilylated with TMSCl/Et$_3$N/ZnCl$_2$[4] to produce stereospecifically (Z)-3-methyl-1-(phenylthio)-2-[(trimethylsilyl)oxy]-1,3-butadiene (**1a**).

Room-temperature Diels–Alder reaction of this new diene with maleic anhydride proceeded well as long as the reaction mixture was concealed from light or contained a small amount of diphenyl disulfide.[5] ^{1}H NMR decoupling experiments on the crystalline cycloadduct **2** established that the reaction had proceeded in the expected endo fashion and did furthermore substantiate the Z nature of the starting diene.

While the room-temperature reaction of **1a** with N-phenylmaleimide also proceeded well to give the crystalline adduct **3**

(Table I), less reactive dienophiles failed to give clean reaction products. Consequently, the reactions of **1a** were examined in the presence of Lewis acids. With *p*-benzoquinone and zinc chloride as catalyst, [4 + 2] cycloaddition gave a crude adduct that was cleaved immediately with hydrofluoric acid in acetonitrile to the crystalline ketone **4**. Use of 300-MHz ^{1}H decoupling experiments established the stereochemistry depicted in this structure, thus signifying that protonation of the enol silyl ether had taken place on the convex face of the molecule.

For the even less reactive dienophiles such as methyl vinyl ketone and methyl acrylate, ethylaluminum dichloride was employed as catalyst. The EtAlCl$_2$-catalyzed reaction of diene **1a** with MVK was complete within 20 min at −78 °C in methylene chloride solvent. A quantitative yield of the endo cycloadduct **5** was obtained. As indicated by the criteria of TLC and 300-MHz ^{1}H NMR analysis, the product was a single isomer of high purity.

Hydrofluoric acid assisted cleavage of the enol silyl ether **5** gave two products in a ratio of 5.5:1 whose structures were identified tentatively through 300-MHz ^{1}H NMR decoupling experiments to be compounds **6** and **7**, respectively. Protonation in this case presumably occurs predominately opposite the pseudoaxial phenylthio substituent.

The ethylaluminum dichloride catalyzed reaction of **1a** with methyl acrylate took place at 0 °C to afford a cycloadduct in 90% crude yield. On silyl ether cleavage, a 1.4:1 mixture of (carbomethoxy)cyclohexanones **8** and **9** was generated in 66% isolated
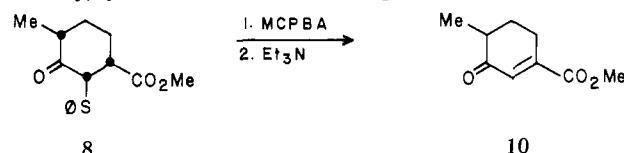
yield. Oxidation of phenylthio group of **8** with MCPBA yielded a sulfoxide which underwent elimination in the presence of triethylamine to give the cyclohexenone **10** in 80% yield, a compound that should itself function as a useful Diels–Alder dienophile.

Of all the reactions we studied with diene **1a**, the α,β-unsaturated aldehydes were found to react in the most startling manner. The EtAlCl$_2$-catalyzed reaction of **1a** with methacrolein was complete within 15 min at −78 °C in methylene chloride as solvent. After a bicarbonate workup and hydrolysis with 5% HCl in acetone to remove the silyl group, a light yellow oil was obtained in 90% yield upon column chromatography. The ^{1}H NMR of this new product showed *no* aldehydic (C(O)*H*) proton. Instead, two sharp methyl singlets and a broad peak at δ 3.73 were found. The IR spectrum revealed a broad absorption at 3420 cm^{-1}. After careful deliberation, it was realized that the Diels–Alder reaction had indeed taken place but that this had been accompanied by a Mukaiyama-like intramolecular aldol condensation[6] to produce **11** on silyl ether cleavage. Europium shift studies indicated that the sterochemistry of the bicyclic was as indicated in the table with the hydroxy group syn to the sulfur substituent, for the H$_{5e}$ and H$_{6e}$ protons moved downfield to almost the same degree as did the H$_{3n}$ proton on addition of increasing amounts of the shift reagent.[7] Mechanistically, this stereochemical result suggests that after the Diels–Alder reaction, the aluminum catalyst may coordinate to both the aldehyde carbonyl and the phenylthio substituent of the cycloadduct to give the six-membered chelate structure **13**, which now undergoes the internal aldol reaction with

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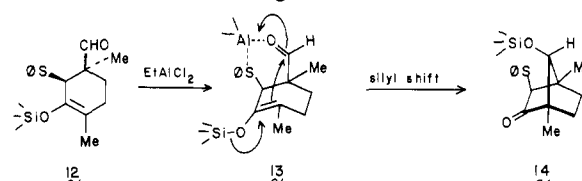
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