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Photochemical Cycloaddition of Singlet *trans*-Stilbene with α,β-Unsaturated Esters

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The photochemical cycloaddition reactions of singlet *trans*-stilbene with five α,β-unsaturated esters and diesters are described. Adduct stereochemistry is influenced more by secondary π-orbital overlap than by steric effects. The reactivity of the unsaturated esters with singlet stilbene increases with their electron affinity. This trend is consistent with the formation of a charge-transfer-stabilized exciplex intermediate in which singlet stilbene is the electron donor. Cycloaddition quantum yields, however, decrease with increasing electron affinity. This trend is readily explained by using simple frontier molecular orbital theory.

Photochemical [2 + 2] cycloaddition reactions of singlet *trans*-stilbene with numerous electron-rich alkenes and dienes have been reported and are known to occur via singlet exciplex intermediates.[1] Quantum yields for these reactions are uniformly high ($\Phi > 0.5$), making them preparatively useful. In contrast, the only cycloaddition reaction of *trans*-stilbene with an electron-poor alkene (dimethyl fumarate) investigated quantitatively is quite inefficient ($\Phi = 0.04$).[2] Furthermore, alkenes more electron deficient than dimethyl fumarate fail to add to *trans*-stilbene, even though they are diffusion-controlled quenchers of singlet *trans*-stilbene.[2] In order to better define the synthetic scope and mechanism of the photochemical cycloaddition process, we have investigated the reactions of singlet *trans*-stilbene with several α,β-unsaturated esters and diesters.

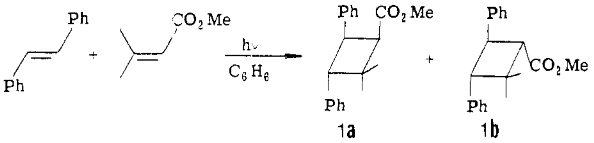
Table I. Quantum Yields for Cycloaddition and Stern-Volmer Quenching Constants

alkene	IP, eV[a]	Φ_∞[b]	$k_q\tau$, M^{-1}[c]
2,5-dimethyl-2,4-hexadiene[d]	7.8	0.83	1.6
2,3-dimethyl-2-butene[e]	8.3	1.0	0.24
methyl 3-methylcrotonate		0.89	0.08
methyl crotonate	10.1	0.96	0.19
dimethyl ethylidenemalonate		0.61	0.41
diethyl isopropylidenemalonate		0.11	1.0
dimethyl dimethylmaleate		0.11	0.96
dimethyl fumarate[f]	10.7	0.04	1.9

[a] Alkene ionization potential. [b] Extrapolated quantum yield (eq 6). [c] Intercept/slope ratio (eq 6). [d] Data from ref 10. [e] Data from ref 7. [f] Data from ref 2.

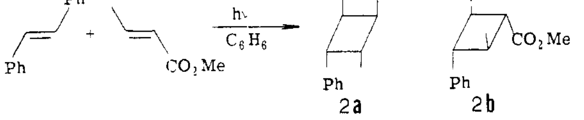
Results

Preparative Photochemistry. Irradiation of a benzene solution of *trans*-stilbene (0.05 M) and methyl 3-methylcrotonate (0.5 M) with Pyrex-filtered light yields two isomeric cycloadducts **1a** and **1b** in a 4.4:1 ratio. Structure assignments are based on comparison of NMR data with those of Hirsch[3] for the same isomers obtained by degradation of *trans*-stilbene-2,5-dimethyl-2,4-hexadiene photoadducts. These adducts are obtained in comparable yields with a **1a**/**1b** isomer ratio of 3.4 in acetonitrile solution. Irradiation of *trans*-stilbene with methyl crotonate yields two isomeric cycloadducts **2a** and **2b** in a 2.0:1 ratio (eq 2). Structure assignments are based on comparison of NMR data with those of Rejtö[4] for samples obtained by esterification of the photoadducts of *trans*-stilbene with crotonic acid. Irradiation of *trans*-stilbene and dimethyl ethylidenemalonate yields two isomeric cycloadducts **3a** and **3b** in a 2.0:1 ratio. The isolated yield of cycloadducts in a typical preparative photolysis was 54%, based on limiting stilbene. Stereochemical assignments are based on NMR data and the known shielding effect of a β-*cis*-phenyl group.[3,5] Irradiation of *trans*-stilbene with diethyl isopropylidenemalonate or with dimethyl dimethylmaleate results in the formation of a single cycloadduct, **4** and **5**, respectively (eq 4 and 5).



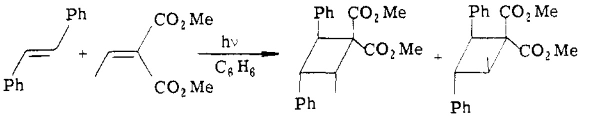
1a 1b

(1)



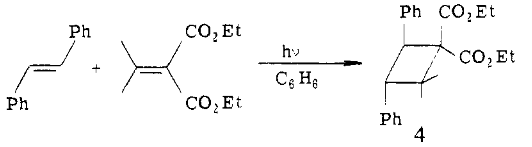
2a 2b

(2)



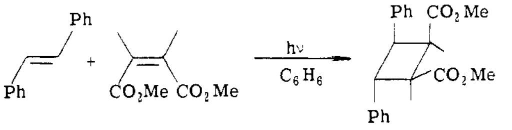
3a 3b

(3)



4

(4)



5

(5)

Quantitative Studies. Quantum yields for cycloadduct formation were determined as a function of unsaturated ester concentration for degassed benzene solutions of *trans*-stilbene (0.05 M) at 26 °C by using monochromatic 313-nm irradiation. Stilbene absorbs >95% of the incident radiation under these conditions. The variation in total cycloadduct quantum yield with reciprocal unsaturated

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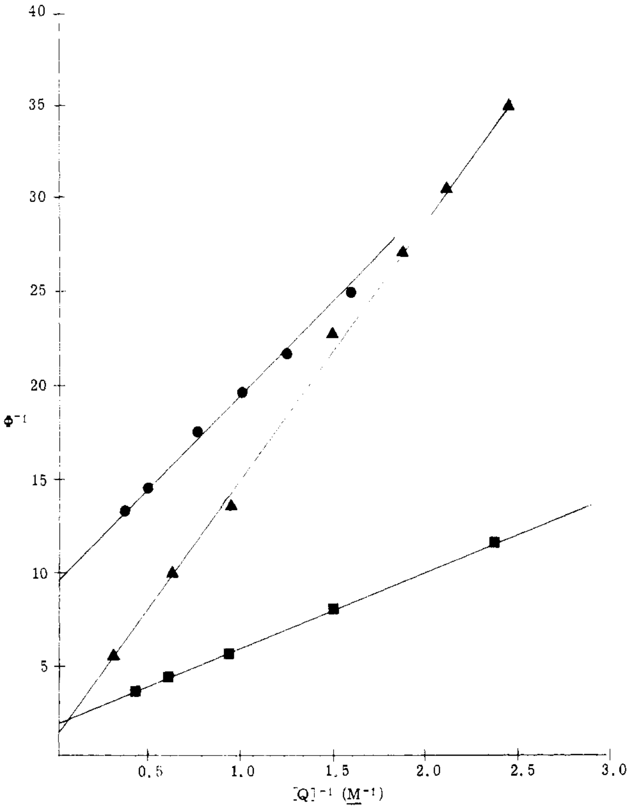

Figure 1. Dependence of cycloaddition quantum yield upon concentration of methyl 3-methylcrotonate (▲), dimethyl ethylidenemalonate (■), and dimethyl dimethylmaleate (●).

ester concentration [A] is shown in Figure 1 for several esters. These plots give acceptable least-squares fits ($r > 0.99$) to the linear eq 6, where Φ_∞ is the quantum yield at

$$\Phi^{-1} = \Phi_\infty^{-1}(1 + (k_q\tau[A])^{-1}) \quad (6)$$

infinite ester concentration and $k_q\tau$ is the Stern–Volmer constant obtained from the intercept/slope ratio.[2] Values of Φ_∞ and $k_q\tau$ for the unsaturated esters investigated are given in Table I along with previously reported values for 2,5-dimethyl-2,4-hexadiene,[6] 2,3-dimethyl-2-butene,[7] and dimethyl fumarate.[2] The substituted alkenes are listed in approximate order of increasing electron affinity.

The fluorescence of *trans*-stilbene (10^{-4} M) is quenched by all of the unsaturated esters investigated. Stern–Volmer plots for fluorescence quenching should, in principle, yield the same $k_q\tau$ values as those obtained from product quantum yield measurements. However, the high ester concentrations required for measurable fluorescence quenching result in competitive absorption of the exciting light (320 nm) by quencher. Competitive absorption does not affect product quantum yield measurements due to the much higher *trans*-stilbene concentrations employed. Exciplex fluorescence was either very weak or nonexistent in all cases.

Discussion

All of the α,β-unsaturated esters investigated react with electronically excited *trans*-stilbene to form [2 + 2] cycloadducts. While these reactions are relatively clean at low conversions, preparative yields are limited to ca. 50% by secondary photoreactions of the cycloadducts.[8] The retention of stilbene and ester stereochemistry and the dependence of cycloadduct quantum yield upon ester concentration (Figure 1) are consistent with a singlet-state reaction. Previous investigations have established the general presence of reversibly formed exciplex intermediates in such reactions.[1-7] The simplest kinetic scheme for exciplex cycloaddition is given in eq 7, where TS and CS are *trans*- and *cis*-stilbene, A is the unsaturated ester, and τ^{-1} and k_d include both radiative and nonradiative decay processes. The Stern–Volmer relationship for adduct formation is given by eq 8, which is of the same form

$$\begin{tikzcd}
\text{TS} \arrow[r, "h\nu"] & \text{TS}^* + \text{A} \arrow[r, shift left, "k_e"] \arrow[d, "\tau^{-1}"] & \text{exciplex} \arrow[l, shift left, "k_{-e}"] \arrow[r, "k_a"] \arrow[d, "k_d"] & \text{adduct} \\
 & \text{TS} + \text{CS} & \text{TS} + \text{A} &
\end{tikzcd} \quad (7)$$

$$\frac{1}{\Phi} = \frac{k_a + k_d}{k_a} + \frac{k_{-e} + k_a + k_d}{\tau k_e k_a[A]} \quad (8)$$

as eq 6 and provides kinetic expressions for $\Phi_\infty[k_a/(k_a + k_d)]$ and $k_q[k_e(k_a + k_d)/(k_a + k_d + k_{-e})]$. The values of Φ_∞ generally decrease as the electron affinity of the unsaturated ester increases. Extrapolation of this trend predicts the reported failure of cycloaddition with alkenes more electron deficient than dimethyl fumarate.[2] Thus the synthetic scope of stilbene [2 + 2] cycloaddition is limited to electron-rich and moderately electron-poor alkenes. The one exception to the trend seen in Table I is dimethyl ethylidenemalonate which forms adducts more efficiently than diethyl isopropylidenemalonate or dimethyl dimethylmaleate. This exception could reflect a small steric effect on the cycloaddition process (vide infra) or on the ground-state conformation of these unsaturated esters.[9]

The reactions shown in eq 1 and 2 both yield cyclobutanes with carbomethoxy cis to the adjacent phenyl group as the major isomer. Base-catalyzed equilibration of **1a** and **1b** shows the latter to be more stable by 2.3 kcal/mol.[3] Thus the thermodynamically less stable isomer is formed preferentially, as is the case for cycloaddition of *trans*-stilbene and 2,5-dimethyl-2,4-hexadiene.[3] This preference may be attributed to stabilization of either an exciplex intermediate or the transition state leading to cycloadducts by secondary π-orbital overlap.[5] This preference is more pronounced in the reaction of *trans*-stilbene and dimethyl fumarate, which yields exclusively dimethyl μ-truxinate.[2] The reaction of stilbene with dimethyl ethylidenemalonate (eq 3) yields more **3a** than **3b**, even though the latter isomer would be expected to be more stable. Clearly, steric effects exert, at most, a minor influence on cycloadduct stereochemistry.

The Stern–Volmer constants ($k_q\tau$) for alkene quenching of singlet *trans*-stilbene (Table I) first decrease and then increase with increasing alkene electron affinity. This trend is consistent with the formation of a charge-transfer-stabilized exciplex in which stilbene acts as an electron acceptor (A*) with electron-rich alkenes (D) and as an electron donor (D*) with electron-poor alkenes (A) (eq 9).

$$\begin{tikzcd}
\text{A}^* + \text{D} \arrow[dr, shift left] & & \\
\text{or} & \text{exciplex} \arrow[ul, shift left] \arrow[dl, shift left] \arrow[r] & \text{cycloadducts} \\
\text{D}^* + \text{A} \arrow[ur, shift left] & &
\end{tikzcd} \quad (9)$$

Weak exciplex emission has been observed from singlet

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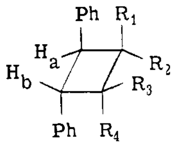
Table II. NMR Data for Cycloadducts[a]



adduct	chemical shift (J)					
	R_1	R_2	R_3	R_4	H_a	H_b
1a	3.35	4.2 (4.0)	1.26	0.94	3.81 (4.0, 4.2)	4.2 (4.2)
1b	2.91 (10.4)	3.70	1.43	0.75	4.2	3.43 (11.1)
2a	3.27			0.93 (8)		
2b		3.63	1.27 (5)			
3a	3.22	3.72		0.78 (7.6)		
3b	3.32	3.78	1.34 (6.6)			
4	3.74[b]	4.30[b]	1.50	0.81	4.59 (12)	4.33 (12)
5	3.21	1.55	3.68	1.05	4.87 (14)	3.72 (14)

[a] All spectra in $CDCl_3$. Chemical shifts are in parts per million from Me_4Si and coupling constants in Hz. [b] Methylene protons. Methyl protons in R_1 and R_2 are at δ 0.84 and 1.30, respectively ($J = 7.5$ Hz).

stilbene exciplexes with 2,5-dimethyl-2,4-hexadiene[10] and dimethyl fumarate[2] but not with the other quenchers in Table I. It is reasonable to assume that singlet exciplexes are intermediates in all of the cycloaddition reactions of singlet *trans*-stilbene and that the failure to observe fluorescence is due to a very short exciplex lifetime (<1 ns).

The most striking finding of the present investigation is the inverse relationship between alkene reactivity ($k_q\tau$) and cycloaddition efficiency (Φ_∞, Table I). Reactivity is primarily determined by the stability of the exciplex intermediate, which is dependent upon the extent of charge transfer.[1] Energies of the highest occupied (HO) and lowest unoccupied molecular orbitals of *trans*-stilbene, methyl crotonate, and dimethyl fumarate estimated from electrochemical and ionization potential data are shown in Figure 2.[2,12] Electron transfer from singlet *trans*-stilbene to methyl crotonate and dimethyl fumarate is seen to be slightly endothermic and highly exothermic, respectively. Thus a more stable exciplex should be formed in the latter case, as is observed. On the other hand, cycloaddition is predicted by frontier molecular orbital (FMO) theory to be most efficient when the interacting frontier orbitals are nearly isoenergetic.[11] Thus FMO theory predicts more efficient stilbene cycloaddition with methyl crotonate than with dimethyl fumarate (Figure 2), as is observed (Table I). While FMO theory ignores the details of exciplex formation and exciplex cycloaddition,[1,13] we have found it to be highly useful in predicting the efficiency and stereochemistry of symmetry-allowed singlet-state cycloaddition reactions.[1]

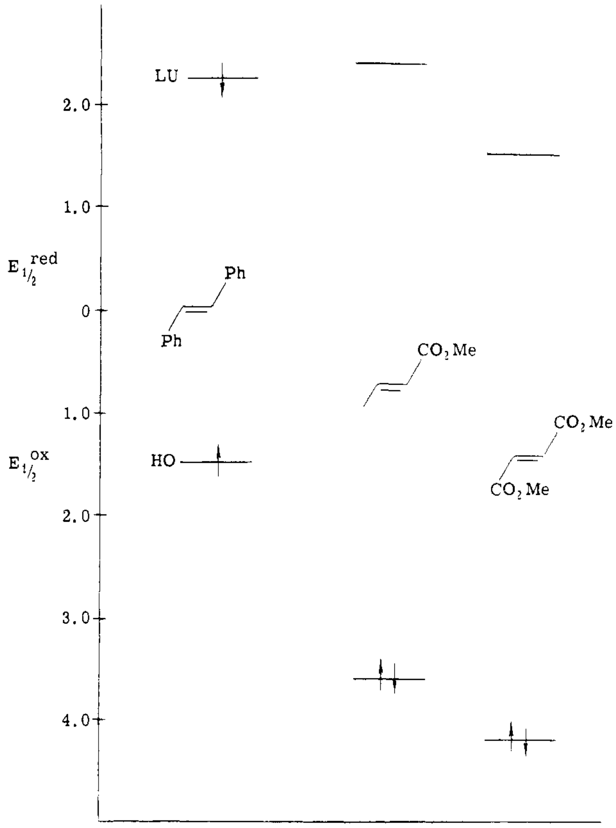


Figure 2. Frontier orbital energies estimated from electrochemical oxidation ($E_{1/2}^{oxidn}$) and reduction ($E_{1/2}^{redn}$) potentials.

Experimental Section

General Procedures. *trans*-Stilbene (Aldrich) was recrystallized from benzene and from ethanol. Spectrograde benzene (Aldrich) was distilled from P_2O_5 and from Na/benzophenone under N_2. Methyl crotonate (Aldrich) was fractionally distilled prior to use. Diethyl isopropylidenemalonate,[14] dimethyl ethylidenemalonate,[14] and dimethyl dimethylmaleate[15] were prepared by literature methods. Methyl 3-methylcrotonate was prepared by esterification of 3-methylcrotonic acid (Aldrich) and fractionally distilled prior to use.

Quantum yield measurements were carried out by using a Hanovia 450-W medium-pressure mercury lamp in a water-cooled Pyrex immersion well. Monochromatic light (313 nm) was provided by a potassium chromate filter solution in a Pyrex lamp well. *trans*-Stilbene to *cis*-stilbene conversion was used as an actinometer ($\Phi_{t\to c} = 0.50$).[16] Samples were prepared by using benzene solutions (3 mL) of *trans*-stilbene (0.05 M) and quencher in 13-mm-o.d. Pyrex ampules which were degassed by three freeze-pump-thaw cycles and sealed under vacuum. Samples were irradiated on a merry-go-round apparatus maintained at a temperature of 26 ± 2 °C, and analyzed by GC on a 3 ft × $^1/_8$ in. column of 5% SF96 on Chromosorb G.

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Preparative photolyses were generally carried out in benzene (50–100 mL) by using 0.05 M *trans*-stilbene and 0.5 M ester. Samples were degassed prior to irradiation through Pyrex with a 450-W medium-pressure mercury lamp by bubbling dry nitrogen through the solution for 10–15 min. Reaction progress was monitored by GC. Yields were not optimized. The isolated yield of cycloadducts from the *trans*-stilbene–dimethyl ethylidenemalonate reaction mixture is representative of the reactions studied.

Methyl 4,4-Dimethyl-*c*-2,*t*-3-diphenylcyclobutane-1-carboxylate (1a) and Methyl 4,4-Dimethyl-*t*-2,*c*-3-dicyclobutane-1-carboxylate (1b). The *trans*-stilbene–methyl 3-methylcrotonate reaction mixture was chromatographed on alumina with 0–1% ethyl acetate in hexane as eluant. The major adduct, **1a**, eluted after the stilbenes and was isolated as a 6:1 mixture of **1a** and **1b**. **1b** followed and was isolated as a 1:1 mixture of **1a** and **1b**: the NMR data (Table II) are consistent with those reported by Hirsch;[3] IR (CCl_4, mixture of isomers) 5.75, 7.91 μm.

Methyl *t*-4-Methyl-*c*-2,*t*-3-diphenylcyclobutane-1-carboxylate (2a) and Methyl *t*-4-Methyl-*t*-2,*c*-3-diphenylcyclobutane-1-carboxylate (2b). The *trans*-stilbene–methyl crotonate reaction mixture was chromatographed on alumina with 2% ethyl acetate in hexane as eluant. Attempted crystallization of the isomeric mixture was unsuccessful: the NMR data in Table II is consistent with that reported by Retjö;[4] IR (CCl_4, mixture of isomers) 5.76, 8.55 μm.

Dimethyl *r*-2,*t*-3-Diphenyl-*t*-4-methylcyclobutane-1,1-dicarboxylate (3a) and Dimethyl *r*-2,*t*-3-Diphenyl-*c*-4-methylcyclobutane-1,1-dicarboxylate (3b). A solution of *trans*-stilbene (0.45 g) and dimethyl ethylidenemalonate (4.0 g) in 50 mL of benzene was irradiated 38 h. The solvent was removed, the unreacted ester distilled bulb-to-bulb, and the residue chromatographed on alumina (50 g) with 0–4% ethyl acetate in hexane as eluant. Early product-containing fractions were enriched in the major isomer, **3a**; later fractions were enriched in **3b**. Fractional crystallization afforded no further enrichment of either isomer: yield 0.46 g (54%); NMR (see Table II); IR (CCl_4, mixture of isomers) 5.76, 7.84, 7.97 μm.

Diethyl 4,4-Dimethyl-*t*-2,3-diphenylcyclobutane-1,1-dicarboxylate (4). The *trans*-stilbene–diethyl isopropylidenemalonate reaction mixture was chromatographed on silica gel with 5% ethyl acetate in hexane as eluant. Stilbenes eluted first, followed by **4**. The crude product was recrystallized from hexane: mp 124.5–125 °C; NMR (see Table II).

Dimethyl 1,2-Dimethyl-*t*-3,4-diphenylcyclobutane-*c*-1,2-dicarboxylate (5). The *trans*-stilbene–dimethyl dimethylmaleate reaction mixture was chromatographed on alumina with 0–2% ethyl acetate in hexane as eluant. The crude product was recrystallized from hexane: mp 104.9–105.2 °C; NMR (see Table II); IR (KBr) 5.74, 5.83 μm.

Registry No. 1a, 72727-30-1; **1b**, 72777-29-8; **2a**, 72727-31-2; **2b**, 72777-30-1; **3a**, 72727-32-3; **3b**, 72777-31-2; **4**, 72727-33-4; **5**, 72727-34-5; *trans*-stilbene, 103-30-0; methyl 3-methylcrotonate, 924-50-5; methyl crotonate, 18707-60-3; dimethyl ethylidenemalonate, 17041-60-0; diethyl isopropylidenemalonate, 6802-75-1; dimethyl dimethylmaleate, 13314-92-6.

Photochemical Transformations. 26. Sensitized and Unsensitized Photoreactions of Some Benzyl Chlorides in *tert*-Butyl Alcohol[1]

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Benzyl chloride and a variety of meta- and para-substituted derivatives have been irradiated in *tert*-butyl alcohol at 254 nm or in acetone–*tert*-butyl alcohol mixtures at 300 nm. Quantum and chemical yields of photosolvolysis products (benzyl *tert*-butyl ether and/or benzyl alcohol), photohomolysis products (bibenzyl and 4-phenyl-2-methyl-2-butanol), and corresponding products from substituted benzyl chlorides have been measured as functions of substrate concentration and medium composition. Sensitized reactions favor bond heterolysis, but direct irradiations favor homolysis, although reactions are not clean in either case. There is no correlation between quantum yields for photosolvolysis and Hammett σ or Brown σ^+ constants, and no salt effects of added lithium perchlorate were observed, in either direct or sensitized reactions.

In the decade and a half following the report[2] by Zimmerman and Sandel of the photosolvolysis of certain benzyl derivatives, that is, photochemically induced bond heterolysis, there has been a considerable amount of work on the photochemistry of benzyl compounds in nucleophilic solvents. The compounds studied include benzyl (or substituted benzyl) sulfonium salts,[3] ammonium salts,[4-6] acetates,[2,7,8] phosphonium salts,[9] and halides,[2,10-13] and it has been reported that products resulting from both heterolysis and homolysis of the benzyl–heteroatom bond are formed either upon direct irradiation or upon photosensitization.

The proportion of homolytic and heterolytic cleavage depends on the nature of the leaving group in the molecule and on the apparent multiplicity of the excited state (direct irradiation vs. photosensitization), but how these factors influence the choice of cleavage type is not yet clear. We

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