Table I. Comparison of Enone Conformational Preferences with Product Enolate Ratios

		enone 1			approx enone ratio[a]	enolate ratio[a,b]	yield[c]
	R^1	R^2	R^3	R^4			
a	i-Pr	H	H	n-Hex	>20:1	170:1[d]	69%
b	Ph	H	H	n-Hex	>20:1	100:1[d]	96%
c	n-Pr	H	H	i-Pr	>20:1	50:1[d]	83%
d	H	n-Bu	H	n-Hex	3:1	2:1[e]	71%
e	H	n-Bu	H	t-Bu	<1:100	<1:300[e]	85%
f	H	H	n-Bu	n-Hex	1:20	1:30[e]	68%
g	H	H	n-Bu	i-Pr	<1:100	1:300[e]	82%
h	Me	Me	Me	n-Hex	1:3	1:4[e]	91%

[a] s-trans:s-cis 2:3, estimated from published calculations and experimentally determined ratios.[5] [b] Determined by silylation and capillary GC of the resulting crude mixture. [c] Internal standard GC yield. The remainder generally consists of 10–25% of the simple saturated ketone. [d] Reduction with L-Selectride. [e] Reduction with Li/NH₃.

conformer is known to be controlled by the specific substitution pattern on the double bond (R^1, R^2, R^3) and in the α'-position (R^4).[5] In general, an alkyl substituent in the α-position (R^1 = alkyl, R^3 = H) causes the s-trans conformer to be favored, while one in the cis β-position (R^3 = alkyl) shifts the ratio in favor of s-cis. A trans β-substituent has little effect upon the ratio, but increased branching in the α'-position (R^4) results in an increased preference for the s-cis enone regardless of other substituents. We felt it might be possible to use these conformational generalizations to predict which of the two enolate stereoisomers should predominate for any specific substitution pattern. Mindful of the fact that conformer reactivities and interconversion rates, embodied in the Curtin–Hammett Principle, could well render this simple hypothesis invalid, we have tested eight representative acyclic enones and found that the model is indeed a useful one.

The first example was chosen such that the s-trans conformer would be strongly preferred in the ground state.[6] Reduction of **1a** (Table I) with L-Selectride[4a] (Aldrich) (THF, –78 °C, 15 min) followed by silylation (Me₃SiCl/Et₃N,[7] –78 → –10 °C) gave a mixture of silyl ethers, corresponding to **2a** and **3a**, in a ratio of 170:1 (69% yield) as determined by capillary GC analysis of the crude reaction mixture.[8] As expected, increasing the steric bulk at R^4 and decreasing it at R^1 results in a reduction in stereoselectivity (see **1c**), from 170:1 to 50:1. The corresponding α-phenyl enone (**1b**) gave a similar result (100:1, 96% yield). Determination of the stereochemistry of the major isomer in these examples and others was readily made by 250-MHz proton difference NOE analysis.

In contrast to these three enones, **1f** exists mainly in the s-cis ground-state conformation. Although L-Selectride gave predominantly 1,2-reduction of **1f**, dissolving metal reduction and silylation (excess Li/NH₃, –78 °C; isoprene; replace NH₃ with THF at –10 °C; Me₃SiCl, Et₃N) gave a 1:30 mixture of **2f** and **3f** (68% yield), again in accord with the simple conformational hypothesis.[9] Once again, increasing steric bulk of R^4 shifts the conformational equilibrium toward s-cis, so that the reduction of

1g is considerably more selective (1:300) than it is for **1f**. It should be noted that the predominant enolates in these cases (**3**), which are thermodynamically more stable than their geometric isomers, cannot be generated nearly as selectively by more conventional methods.[1] As further confirmation of the predictive power of the stereochemical hypothesis, reduction of **1e**, for which the s-cis conformer heavily predominates, produces exclusively (<1:300) the enolate **3**.

Several other results also proved to be consistent with the simple model. Two enones in the table show little conformational preference: **1d** because of a lack of "controlling" substituents (R^1, R^3, or bulky R^4) and **1h** because of a competition between controlling substituents (R^1 and R^3). The reduction of these enones thus is expected to be relatively nonselective, and the slight s-trans preference of **1d** results in only a 2:1 enolate ratio. Furthermore, **1h** gives a 1:4 enolate ratio that reflects the fact that the R^3 substituent predominates—but only slightly—over an identical R^1 substituent in determining the conformer populations.

A knowledge of enone ground-state conformational preferences thus does allow one to predict which enolate geometrical isomer will predominate in these reactions. On the basis of the representative examples described in this paper, a wide range of enolates that are highly substituted or otherwise difficult to generate selectively are now readily available.

Supplementary Material Available: General procedures for the preparation of starting enones, representative conjugation reduction procedures, and spectra for product silyl enol ethers (10 pages). Ordering information is given on any current masthead page.

(6) For 3-methyl-3-buten-2-one the s-trans:s-cis ratio is reportedly 13:1.[5] This ratio is expected to be even greater when the R^1 group is larger than the R^4 group (isopropyl vs. n-hexyl).[5]
(7) Previously centrifuged to remove triethylamine hydrochloride.
(8) All silyl ethers exhibited satisfactory 250-MHz proton NMR spectra and high-resolution mass spectra (of individual isomers by GC/HRMS). Authentic samples of extremely minor isomers were prepared by allowing enolate mixtures to equilibrate before silylation. Where applicable, authentic product mixtures were prepared by standard methods.
(9) The mechanisms of conjugate reduction by L-Selectride and Li/NH₃ obviously are different; however, in both cases the product enolate geometry is established when electron density is increased in the enone π* orbital either by electron transfer or hydride attack at the β-position. In either reaction the bond order between C-2 and C-3 (the incipient enolate π-bond) increases as the reaction progresses, which eventually "locks" the geometry of the resulting double bond. L-Selectride is the more convenient of the two reagents, and it gives a slightly better enolate ratio than does Li/NH₃, at least in the case of **1c** (50:1 vs. 10:1). This minor discrepancy may reflect the different reduction mechanisms involved, but it does not detract from the overall predictive value of our conformational hypothesis (e.g., compare **1d** to **1f**).

Picosecond Dynamics of the Excited *trans*-Stilbene/Fumaronitrile Charge-Transfer Complex

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The coupling of the molecular motions of solvent and reactant molecules in photochemical reactions has been of considerable interest.[1] We report the use of picosecond absorption spectroscopy to examine the "microdynamics"[2] of the excited *trans*-stilbene/fumaronitrile charge-transfer complex.[3–5] In particular, we can measure the absolute rates of ion pair separation.

The experimental procedure for obtaining absorption spectra of transient intermediates with a time resolution of 25 ps has been previously described in detail.[6] Irradiation was performed with 355-nm pulses at room temperature on 0.05 M *trans*-stilbene/0.3 M fumaronitrile (TS/F) solutions. The irradiated solutions were rapidly stirred and frequently changed to prevent the buildup of photoproducts.

Excitation of the charge-transfer band of the TS/F complex in several different solvents generates a transient within the laser pulse which is assigned to the radical cation of *trans*-stilbene (TS⁺·(A), λ_{max} = 478 nm)[7] (Figure 1). Although the λ_{max} of

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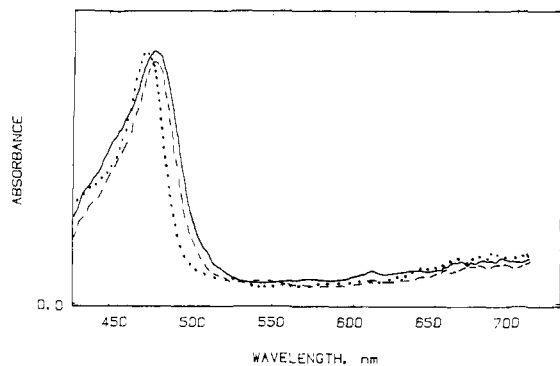
Figure 1. Normalized spectra obtained from the photolysis of TS/F complex in acetonitrile at 355 nm: $TS^+\cdot(A)$ O ps (—), $TS^+\cdot(B)$ 1.85 ns (---), $TS^+\cdot(C)$ 50 ns (···).
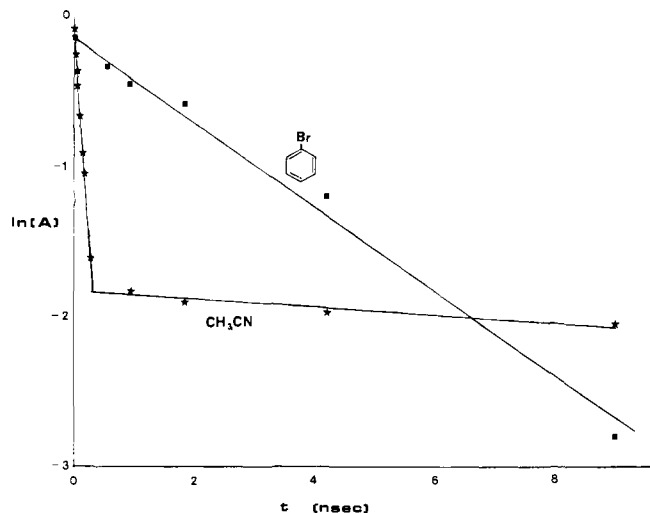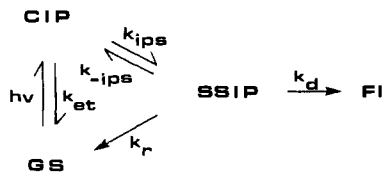

Figure 2. Plot of ln (A) of $TS^+\cdot$ against time in bromobenzene (■) and acetonitrile (☆) after photolysis of TS/F complex at 355 nm. The absorbances were measured at the λ_{max} of $TS^+\cdot$.

$TS^+\cdot(A)$ does not change with solvent, the peak narrows with increasing solvent polarity. In nonpolar solvents (DME and chloro- and bromobenzene), $TS^+\cdot(A)$ decays completely (>97%) by first-order kinetics as monitored by absorption spectroscopy at several wavelengths. In polar solvents (Me_2SO, CH_3CN, acetone, 2-butanone), $TS^+\cdot(A)$ decays by first-order kinetics, but not completely (~75%), as is observed in nonpolar solvents (Figure 2). Transient $TS^+\cdot(A)$ gives rise to a new transient, $TS^+\cdot(B)$, which has a narrower absorption spectrum but the same λ_{max} as $TS^+\cdot(A)$. On the nanosecond timescale, transient $TS^+\cdot(B)$ then undergoes a slow first-order decay (~10% of total signal) and also gives rise to a new transient, $TS^+\cdot(C)$, with a $\lambda_{max} = 472$ nm.

A plausible kinetic scheme to explain the observed decay of $TS^+\cdot(A)$ and $TS^+\cdot(B)$ in the various solvents is shown below. In

$$\text{CIP} \quad \overset{k_{ips}}{\underset{k_{-ips}}{\rightleftharpoons}} \quad \text{SSIP} \quad \overset{k_d}{\longrightarrow} \quad \text{FI}$$
$$hv \Big\downarrow\Big\uparrow k_{et} \qquad\qquad\qquad \searrow k_r$$
$$\text{GS}$$

this scheme, CIP is the contact ion pair of TS/F formed within the laser pulse by excitation of the ground-state complex (GS), SSIP is the solvent-separated ion pair, and FI is the free ions. The rate constant k_{et} is the rate of back electron transfer from the CIP to the GS, k_{ips} is the rate of ion pair separation of the CIP, k_{-ips} is the rate of reformation of the CIP from the SSIP, k_d is the rate of diffusion of the SSIP to FI, and k_r is the summation of the rates of various other decays from SSIP to GS. Similar kinetic schemes have been proposed by Lewis for the addition of amines to TS[1b] and by Peters for the photoreduction of benzophenone.[8] In all

Table I. Comparison of k_{et} with the E_t Value of Various Solvents

solvent	$10^{-8}k_{et}$, s^{-1} [a]	E_T, kcal/mol [b]
benzene	0.8 [c]	34.5
chlorobenzene	3.0	37.5
bromobenzene	2.9	37.5
dimethoxyethane (DME)	5.3	38.2
acetone	21.3	42.2
dimethyl sulfoxide (Me_2SO)	51.0	45.0
acetonitrile	75.8	46.0
1-propanol	107.1	50.7
ethanol	166.6	51.9

[a] ±25%, measured at 300 K. [b] See ref 10. [c] See ref 3.

these mechanisms, pronounced solvent effects and divergent chemical reactivity are attributable to the formation and reaction of these different reactive intermediates.

Excitation of the charge-transfer band of GS, coupled with the spectral absence of the singlet exited state of TS ($\lambda_{max} = 585$ nm)[9] strongly suggests that the CIP is initially formed by electron transfer. Transient $TS^+\cdot(A)$ is assigned to $TS^+\cdot$ in the CIP and its spectral decay most probably corresponds to the back electron transfer (k_{et}) (Table I). Previous work[3–5] indicates that fluorescence and/or the formation of triplet TS do not contribute significantly to the decay of the excited TS/F charge-transfer complex. The rate of back electron transfer increases as the energy separation between CIP and GS decreases. A plot of ln (k_{et}) against the empirical solvent polarity parameter E_T for the various solvents is linear ($r = 0.971$).

In nonpolar solvents (low E_T), $k_{et} > k_{ips}$, and the CIP decays by back electron transfer before ion pair separation occurs. In polar solvents (high E_T), $k_{et} \simeq k_{ips}$, and both back electron transfer and ion pair separation are observed.[11] Transient $TS^+\cdot(B)$ is assigned to $TS^+\cdot$ in the SSIP.[12] The rate and extent of the spectral decay of $TS^+\cdot$ in the CIP does not change with fumaronitrile concentration (0.1–0.3 M), which suggests that transient $TS^+\cdot(B)$ is not formed by an electron hopping mechansim.[13] Assuming similar extinction coefficients for $TS^+\cdot$ in both the CIP and the SSIP, k_{ips} can be obtained from the equation $k_{ips} = [a/(1-a)]k_{et}$, where a is the fraction of $TS^+\cdot(A)$ that undergoes ion pair separation to $TS^+\cdot(B)$. In CH_3CN, $1/k_{ips} = 450 \pm 175$ ps. The spectral evolution of $TS^+\cdot(B)$ to transient $TS^+\cdot(C)$ represents the further separation of the SSIP to form FI (k_d). The first-order decay of the SSIP then corresponds to the summation of the other relaxation pathways of SSIP $(k_{ips} + k_r)$.

The use of picosecond absorption spectroscopy has provided valuable insight into the dynamics of ion pair interchange. Further studies on TS charge-transfer complexes will quantitatively examine the importance of solvent dynamics in TS photochemical reactions.

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(11) In alcoholic solvents, $TS^+\cdot(B)$ decays without significant formation of $TS^+\cdot(B)$ (<5%). Solvent reorganization is slow in alcohols due to hydrogen bonding. Consequently, the rate of ion pair separation is slowed, and back electron transfer predominates.

(12) Alternatively, transient $TS^+\cdot(B)$ may be assigned to the triplet exciplex so the rate k_{ips} becomes the rate of intersystem crossing. In *tert*-butyl alcohol ($E_T = 43.9$) and CH_3CN ($E_T = 46.0$), the rates of intersystem crossing should be similar. However, $k_{ips}(CH_3CN)$ is at least 10 times faster than $k_{ips}(tert$-butyl alcohol).

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