

PHOTOCHEMICAL ADDITION OF STILBENE TO DIENES^{1a}

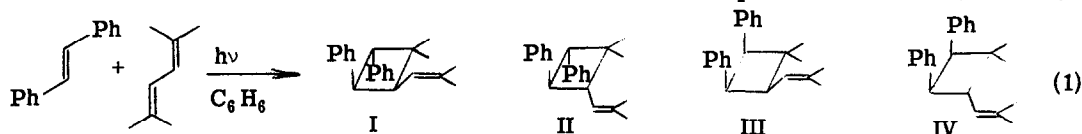
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trans-Stilbene undergoes photochemical [2+2] cycloaddition to simple olefins² and vinyl ethers.³ Addition proceeds from the excited singlet state of stilbene; however both concerted² and nonconcerted³ mechanisms have been suggested. In view of the ability of dienes to quench the fluorescence and form cycloadducts with excited aromatic molecules,⁴ it seemed likely that dienes should also react with stilbene. We find that a variety of dienes add to trans-stilbene and that the rate constants for fluorescence quenching correlate with diene ionization potential.

Irradiation of either cis- or trans-stilbene in the presence of 2,5-dimethyl-2,4-hexadiene (DMH) results in stilbene isomerization and the formation of only two of the four possible cycloadducts (eq 1). The product ratio (55:45 by gc) was independent of initial stilbene stereochemistry or extent conversion. Plots of reaction mixture composition vs. irradiation time



show that cycloaddition and isomerization are both primary processes for trans-stilbene (Figure 1), but that isomerization precedes cycloaddition for cis-stilbene (Figure 2). Irradiation of cis- or trans-stilbene and DMH in the presence of Michler's ketone leads to stilbene isomerization, but not to cycloadduct formation. Thus addition occurs only to the excited singlet state of trans-stilbene as is the case for simple olefins.²

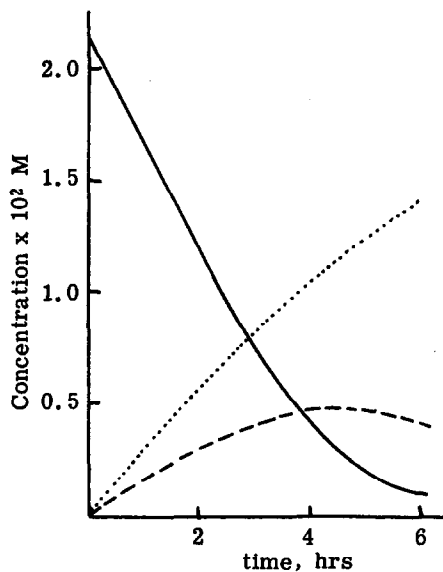


Figure 1. Isomerization of trans (—) to cis (---) stilbene and adduct formation (···).

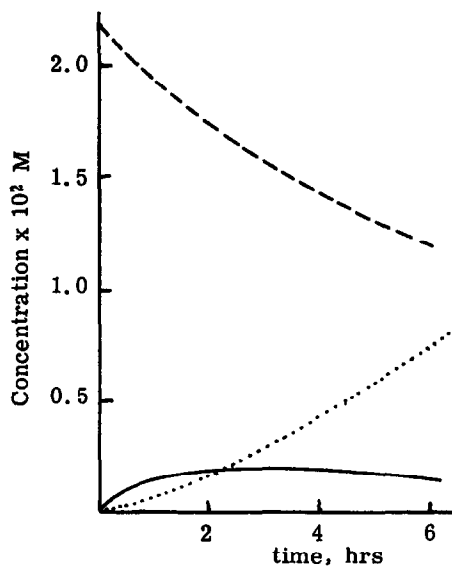
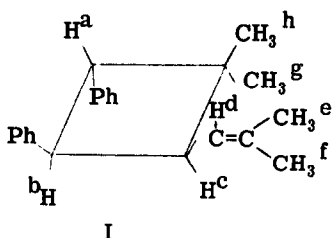


Figure 2. Isomerization of cis (---) to trans (—) stilbene and adduct formation (···).

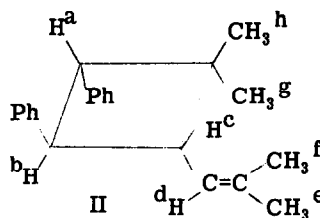
The two photoadducts were separated by fractional crystallization. The minor product was obtained as a crystalline solid (mp 78-79°; Anal. Calcd. for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 90.75; H, 9.17) and the minor product as a colorless oil. Both adducts were recovered unchanged after heating with *t*-butoxide in DMSO, conditions reported to convert cis-diphenylcyclobutanes to the more stable trans isomers.^{3b, 5} The absence of isomerization along with the observation that the adducts form only with trans-stilbene is suggestive of trans phenyl stereochemistry (I and II).

The nmr spectra of both adducts show two ring methyls, two olefinic methyls, and an AMX pattern for the three ring protons.⁶ Tentative assignment of trans, cis stereochemistry (I) to the major adduct and all-trans stereochemistry (II) to the minor adduct is based on the known shielding effect of β -cis-phenyl groups on protons and methyl groups.^{5, 7} The chemical shift of H_C is 0.2 ppm upfield in adduct II vs. I, whereas the opposite effect is observed for the vinyl proton H_D .

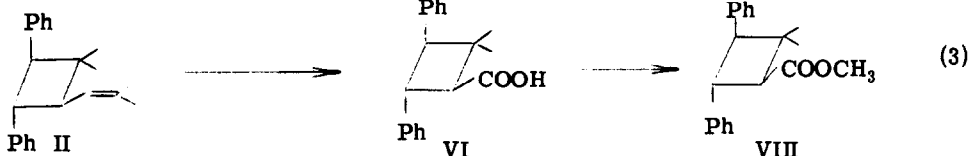
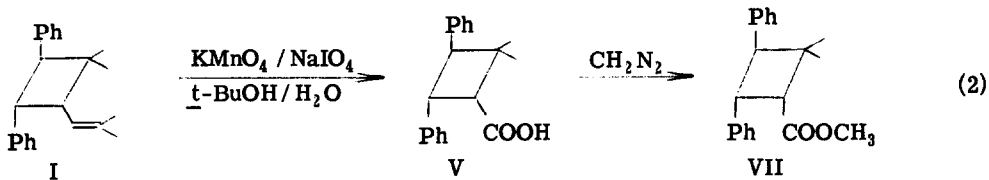
Stereochemical assignments for I and II were verified by two degradative schemes. Oxidative cleavage of the olefinic side chain either with ozone or permanganate/periodate⁸ yields the crystalline acids V and VI which were converted to the corresponding esters VII and VIII by reaction with diazomethane (eq 2, 3). Treatment of VII or VIII with 0.1 M methoxide



a 3.60 (d, $J_{a,b} = 11.1$)
 b 4.15 (q, $J_{a,b} = 11.1$, $J_{b,c} = 9.0$)
 c 3.03 (q, $J_{b,c} = 9.0$, $J_{c,d} = 10.2$)
 d 5.06 (d, $J_{c,d} = 10.2$)
 e, f 1.56 (s)
 g 0.92 (s)
 h 1.06 (s)

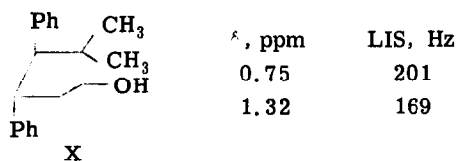
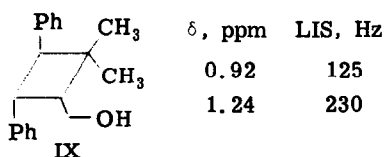


a 3.25 (d, $J_{a,b} = 10.8$)
 b 3.53 (q, $J_{a,b} = 10.8$, $J_{b,c} = 9.2$)
 c 2.80 (q, $J_{b,c} = 9.2$, $J_{c,d} = 9.4$)
 d 5.30 (d, $J_{c,d} = 9.4$)
 e 1.60 (d, $J_{d,e} < 2$)
 f 1.74 (d, $J_{d,f} < 1$)
 g 0.68 (s)
 h 1.25 (s)



results in interconversion of the two esters. Since the ester derived from the minor adduct is more stable ($\Delta G = 2.3$ kcal/mole), we conclude it has the all-trans stereochemistry (VIII).

This assignment is corroborated by the effect of the shift reagent $\text{Eu}(\text{FOD})_3$ ⁹ on the nmr spectra of the alcohols IX and X derived from I and II by ozonolysis followed by reductive work-up. The methyl cis to phenyl is at higher field for both adducts.⁷ The upfield methyl experiences the larger lanthanide-induced shift (LIS using 0.9 equiv $\text{Eu}(\text{FOD})_3$) for X, whereas the opposite is observed for IX.



The fluorescence of trans-stilbene is quenched by DMH and other dienes. From the slopes of linear Stern-Volmer plots ($k_q \tau$) and the singlet lifetime of trans-stilbene ($\tau = 2.0 \times$

10^{-10} sec),^{2b} the rate constants for quenching by diene (k_q) can be calculated (Table I). The value of k_q increases with decreasing diene ionization potential as is the case for fluorescence quenching of aromatic hydrocarbons.⁴ The correlation with ionization potential is suggestive of charge transfer from the diene ground state to singlet stilbene. The stereo- and regioselectivity of the cycloaddition of trans-stilbene to other dienes is currently under investigation.

Table I. Kinetic Data for trans-Stilbene Fluorescence Quenching.

Quencher	$k_e \tau^a, M^{-1}$	$k_e \times 10^{-9}, M^{-1} \text{ sec}^{-1}$	IP, eV ^b
2,4-dimethyl-2,4-hexadiene	1.89	9.5	7.84
<u>trans</u> , <u>trans</u> -2,4-hexadiene	1.85	9.3	8.17
<u>cis</u> -1,3-pentadiene	0.67	3.4	8.65
2-methyl-1,3-butadiene	0.45	2.6	8.85

^aSlopes of fluorescence quenching plots in degassed benzene solution. ^bVertical ionization potentials for dienes from ref. 4.

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