values are on the order of 1 M^{-1} and, surprisingly, are more or less independent of structure of the R group.[9] Thus, at low $[Br^-]$, $(1 + K_2[Br^-])$ approaches unity, and eq 9 can be rewritten to show that a plot of $k_{obsd}(1 + K_1[Br^-])$ vs. $[Br^-]$ should yield a straight line with slope of $k_{3A}K_2 = k_{3B}K_1$. The values obtained in this way are listed in Table I.

Methyl for hydrogen substitution at the α carbon results in a large rate acceleration: apparently the electron-donating alkyl inductive effect helps assuage an electron deficiency which develops at the reaction center during electrophilic cleavage by the highly electronegative halogen.[10] For β branching, the electronic substituent effect is attenuated[11] and should thus result in a smaller rate increase; however, a large rate *decrease* is observed, in line with a steric effect (most probably due to van der Waals repulsion in the bimolecular transition state).

The present reaction occurs with retention of configuration[12] and, hence, might have been expected to exhibit an α-branching steric effect, consistent with other front-side cleavages.[13,14] In order to reconcile the experimental data in terms of a single mechanism, it is concluded that an α-steric effect does operate but is masked by an opposing very large electronic effect. For the case of β branching, the now reduced electronic effect is overshadowed by a continued large steric effect (perhaps more severe than for α branching), which is unusual for a retention reaction.[15] Branching at the γ carbon results in a small rate increase, again in the direction of a dominating electronic effect (which should be much attenuated at this position, so that any steric effect must now be very small).

It should be noted that the data do not permit a differentiation between the two kinetic terms possible for one-anion catalysis (eq 5).

Only limited and usually incomplete structure-activity data are available for S_E2 reactions. For those that have been shown to occur with *retention* of configuration at carbon, an examination of the effect on rate of α branching has yielded predominantly polar sequences[16] and predominantly steric sequences,[13] as well as "mixed" sequences.[17] The results presented herein suggest that the interplay of steric and electronic effects may not be revealed unless an examination of the effect of branching is extended to include the β and γ positions as well.

For those S_E2 reactions that have been shown to occur with *inversion* of configuration at carbon, only steric rate sequences (which exhibit different structural dependencies) have so far been observed.[18,19] However, with the proper selection of system, it may be possible to observe polar (and "mixed") sequences here as well, thus completing the structure-activity spectrum for both S_E2 stereochemical classes.

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Photochemical Formation of *trans*-1-Phenylcyclohexene. Chemical Proof of Structure†

Sir:

In a flash photolysis study of *cis*-1-phenylcyclohexene, a transient has been observed to which the structure of *trans*-1-phenylcyclohexene has been assigned.[1] This structural assignment to the transient was based upon the chemistry that it displayed and upon the insensitivity of its lifetime to the polar nature of the solvent. The short lifetime of this new species in methanol at room temperature, $\tau = 9$ μs, was attributed to a fast thermal trans–cis isomerization. This process is apparently slowed down by lowering of the reaction temperature; using data between +30 and −40 °C, the plot of $\log(1/\tau) = f(1/T)$ gave a straight line, indicating an activation energy of ~7.5 kcal/mol. When the temperature was lowered below −50 °C, the lifetime increased less than that predicted from the Arrhenius plot. Thus, the lifetime in methanol at −70 °C of the postulated trans species is only 500 μs, a value nearly ten times smaller than calculated.[2] This observed shorter lifetime could be due to the involvement of a second deactivation process of the postulated trans species which has a low activation energy and which becomes competitive at this lower temperature.

The product(s) formed via this new process was investigated and we present here new chemical evidence which clearly indicates the formation of *trans*-1-phenylcyclohexene by direct irradiation of its cis isomer.

Upon irradiation of *cis*-1-phenylcyclohexene in neutral methanol (0.02 M) at room temperature, the major process is the [2 + 2] dimer formation (58%);[3] the generation of a methyl ether is of minor importance (3%).[4] When the irradiation is conducted in acidic methanol, the yield of methyl

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† This paper is dedicated to Professor E. Havinga on the occasion of his retirement from the Chair of Organic Chemistry at the University of Leiden.

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Table I. Final Atomic Coordinates

no.	x/a	y/b	z/c	no.	x/a	y/b	z/c
1	0.29740	0.47665	0.16340	13	0.09362	0.39734	0.02452
2	0.34088	0.51791	0.28445	14	0.01082	0.33116	0.01422
3	0.38663	0.58285	0.27890	15	−0.00887	0.31589	0.15221
4	0.39003	0.60679	0.15355	16	0.14066	0.32079	0.28526
5	0.34598	0.56681	0.03189	17	0.21151	0.38924	0.29577
6	0.29874	0.50170	0.03454	18	0.24729	0.40419	0.16270
7	0.24840	0.45617	−0.09599	19	0.38213	0.35875	0.17427
8	0.23872	0.48873	−0.23639	20	0.52278	0.36816	0.29188
9	0.18929	0.43965	−0.36113	21	0.64778	0.32794	0.31230
10	0.04202	0.40549	−0.38490	22	0.63413	0.27846	0.21514
11	0.04970	0.37304	−0.24874	23	0.49807	0.26886	0.09832
12	0.09721	0.42233	−0.12016	24	0.37306	0.30853	0.07819

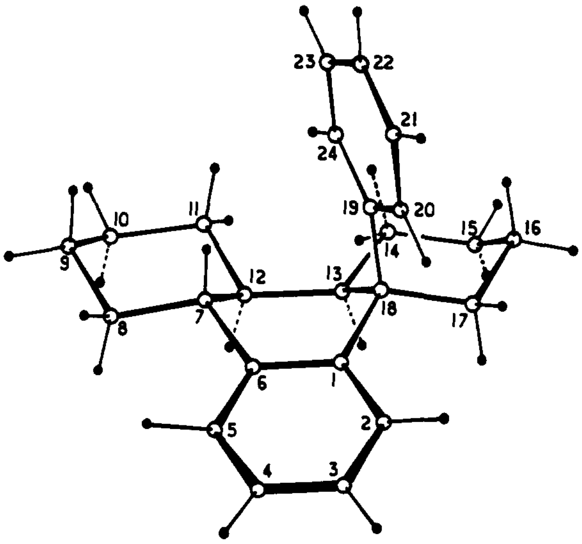


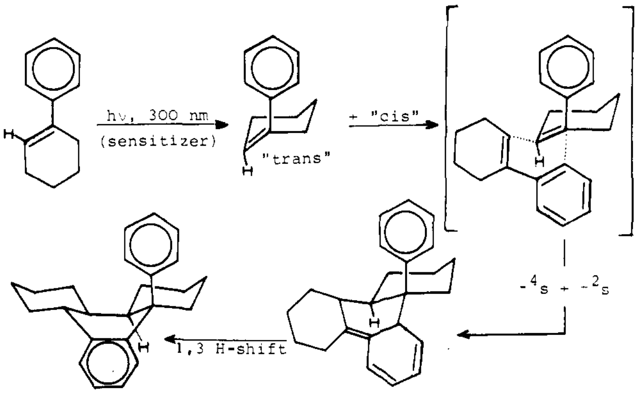
Figure 1. A computer-generated perspective of the material and the numbering scheme.

ether, 1-methoxy-1-phenylcyclohexane, increased (39%).[4] No dimer formation was observed under sensitized conditions.[5] We have now found that, when the irradiation is conducted at a lower temperature, the course of the reaction changes. Direct irradiation of *cis*-1-phenylcyclohexene in neutral methanol (0.023 M, Rayonet photochemical reactor, λ 300 nm) at −75 °C yielded a new dimer in 24% yield at 95% conversion.[6] Under these reaction conditions the yield of the earlier reported [2 + 2] dimer decreased to 6% and the yield of ether increased with respect to values found at room temperature. When the direct irradiation was carried out in acidic methanol, the change in temperature had little effect on the course of the reaction.

Sensitized irradiation (acetophenone, 0.2 M) under the same neutral, low temperature reaction conditions also afforded the new dimer; the yield was 16% at 98% conversion of the starting cis olefin. It also was found that, under these sensitized conditions, the yield of the methyl ether increased with respect to that found in the room temperature reaction.[7]

The new dimer product formed at −75 °C was purified by gas phase chromatography and crystallization (acetone, mp 198–201 °C). The structure of this material was established by X-ray crystallographic analysis. Crystals are monoclinic $a = 9.627$ (2), $b = 20.185$ (5), $c = 10.100$ (2) Å; $\beta = 114.81$ (2)°. Systematic extinctions required space group $P2_1/c$ with four molecules in the unit cell; $d = 1.17$ g/cm^3. The 3436 unique reflections with $\theta < 65°$ were collected on a CAD.4 diffractometer with graphite monochromated Cu Kα X-rays. The structure was solved by direct methods and refined by least-squares procedure to a final conventional residual R value of 0.042 for 2299 observed reflections. The H atoms were included in the calculation. Final atomic coordinates are listed in Table I.

Scheme I



The structure of this new dimer, shown in Figure 1, is the result of a [4 + 2] cycloaddition reaction. This new reaction, occurring only after stabilization of the transient, is believed to be the Woodward-Hoffmann allowed concerted [$_\pi4_s + _\pi2_s$] addition of *cis*-1-phenylcyclohexene to the endocyclic trans double bond of *trans*-1-phenylcyclohexene in the ground state followed by a 1,3-hydrogen shift to yield the product (see Scheme I).

The increased yield of ether under the low temperature conditions favoring reaction of the trans isomer offers experimental evidence to the earlier suggestion of Kropp[4] about the involvement of this strained isomer in the reaction with solvent.

The retained trans stereochemistry at the ring juncture in this dimeric structure is the first stereochemical evidence for the existence of a free *trans*-cyclohexene. This *trans*-1-phenylcyclohexene must be a very reactive dienophile in view of its reaction with a styrene type of molecule at such a low temperature.[8] Reactions of the more stable endocyclic trans double bonds in seven- and eight-membered rings have also been reported to give [2 + 2] as well as [4 + 2] cycloadducts.[9] In the irradiation of cyclohexene in the presence of Cu(I), trans stereochemistry also was observed in [2 + 2] dimers[10] and in a [4 + 2] adduct with butadiene.[11]

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Electronic Spectroscopy of *trans*-Styrylpyridines and Their Conjugate Acids[1]

Sir:

The electronic spectra of the three isomeric *trans*-styrylpyridines and their conjugate acids (referred to as *n*-StP and *n*-StPH$^+$, respectively, where n = 2, 3, or 4) show unusual and hitherto unexplained characteristics.[2-9] We report the results of a new theoretical investigation which support the hypothesis that the bases possess a low-lying $^1n\pi^*$ state.[5,6,8] Our results also indicate that the common assumption that only the $n\pi^*$ states of N heteroaromatics are strongly affected by protonation is not valid for these systems. In particular, protonation changes the lowest $^1\pi\pi^*$ state from an "ethylenic" state into a "charge-transfer" state.

The absorption spectra[2] of these systems appear to be characterized by a strong "ethylenic" band and one or two weaker bands in the same spectral region. Trans-cis isomerization follows excitation to the singlet and triplet manifolds.[3-9] The trans isomers fluoresce with a quantum yield that is strongly system and temperature dependent.[4-6,8] *trans*-3-StP is unusual in that its absorption and fluorescence excitation spectra are different and its isomerization quantum yield is wavelength dependent across the principal absorption band.[9] At least two electronic band systems overlap in this region and the corresponding states appear to be noncommunicating. 3-StPH$^+$ is exceptional in exhibiting fluorescence that is relatively long lived and nonethylenic.[7]

We calculated the spectra of these systems using the all-valence-electron CNDO/S MO model.[10] Pedersen et al.[11] and Distefano et al.[12] have reported CNDO/2 and CNDO/S calculations, respectively, for the bases. Unlike the latter authors, we used the Mataga-Nishimoto[13] formula instead of the Pariser-Parr formula[14] to evaluate the interatomic repulsion integrals because the former locates the singlet states more accurately.[10c] We extended the CNDO/S model to the StPH$^+$'s and performed a complete configuration interaction (CI) calculation between the (49) singly excited $^1\pi\pi^*$ states and a separate CI calculation between the 49 lowest $^1\sigma\pi$ singly excited states.

The calculated absorption spectra are depicted in Figure 1 as vibrationless line spectra superimposed on observed spectra. Observable transitions are indicated by full lines and transitions too weak to show by arrows. Broken arrows denote $^1\sigma\pi$ transitions which are forbidden in the CNDO approximation. Part of the observed spectrum for 3-StPH$^+$ corresponds to a weak, poorly resolved absorption band constructed with reference to the emission spectrum.[7] The lowest $^1\sigma\pi$ state of the StP's is $^1n\pi^*$ in character. The red shift predicted to accompany protonation is overestimated by ~0.4 eV. Similar results have been obtained for the cations of phenazine by Chalvet et al.,[15] who report improved agreement with experiment when the isolated species are replaced by cations hydrogen bonded to water molecules.

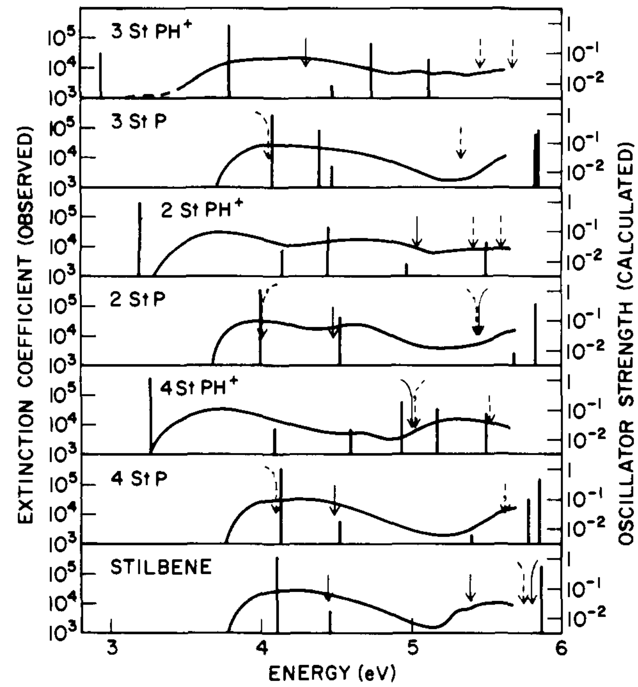

Figure 1. Calculated and observed absorption spectra of stilbene, the three isomeric styrylpyridines, and their conjugate acids. Vertical lines and arrows represent calculated vibrationless line spectra; arrows refer to weak or forbidden transitions. Full and broken arrows denote $^1\pi\pi^*$ and $^1\sigma\pi$ transitions, respectively. The observed spectra are low-resolution, room-temperature spectra taken from the literature.[2-9]

The present CNDO/S model supports the suggestion[5,6,8] that the StP's possess low-energy $^1n\pi^*$ states. These states are calculated to be almost degenerate with the lowest $^1\pi\pi^*$ state, but the accuracy of the model is such that their order in each isomer remains somewhat equivocal.[5,6,8,9,12] The model accounts for the close similarity between the spectra of 4-StP and stilbene, for the emergence of a second strong absorption band at ~4.4 eV in 2-StP, and for the observation[9] of another such band strongly overlapping the first band of 3-StP. It identifies the excited states associated with these transitions in 2- and 3-StP as $^1\pi\pi^*$ states and thus supports Bartocci and Mazzucato's contention that the 3-StP state which they designated S_3 is a $^1\pi\pi^*$ state.[9]

The model is particularly successful in explaining the differences between the spectra of the StPH$^+$'s. The moderate red shift of the principal absorption band, which apparently accompanies protonation of 2- and 4-StP, is replaced in 3-StP by the emergence of a new, much weaker band near 3.3 eV.[7] Protonation of the pyridine ring shifts its MO's to much lower energies. All the π MO's of the StPH$^+$'s, unlike those of stilbene and the StP's, are therefore (1) almost entirely localized on one ring or (2) mainly localized on one ring and one or both of the carbon atoms of the central bond. The wave functions of the lower excited states are dominated by a single configuration. Transitions to these states correspond to a transfer of an electron from the benzene to the pyridinium moiety that is modulated to a greater or lesser degree by the central bond. The final orbital in the lowest energy transition can be de-

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