any degree of certainty to such systems, so that other methods are required for the establishment of geometric relationships.

The question of planarity is less obvious *a priori* in the case of cyclobutanone. Here, compared to the saturated hydrocarbon, the planar form is more stable since the number of eclipsed ethane structures is only two instead of four, and the non-planar form is destabilized by the increased angular strain brought about by the presence of a trigonal ring atom. The result of these effects was examined by an investigation of 2-bromocyclobutanone, obtained by bromination of cyclobutanone. The 2-bromo ketones are a well-studied class of compounds against which all kinds of physical techniques have been brought to bear.[13,14] One of the most useful of such measurements has been dipole moments,[13] which was also employed here. From the known group moments of the carbonyl[15] and the C–Br bond,[16] the moment of 2-bromo-cyclobutanone was calculated assuming a planar ring[17] as 3.43 *D*. The experimental moment in heptane was 3.21 *D*, indicating that the bromine was a little more axial-like than predicted for a planar form. If it is assumed that this moment corresponds to a single axial conformation,[18] the angle between the dipoles can be calculated to be 101°. This fixes also the angle between the dipoles for the corresponding equatorial conformation at 69°, and gives a calculated moment for the latter of 3.85 *D*.

If the bromine is in fact very largely axial in heptane, it would be expected that some of the equatorial form could be detected as the solvent polarity was increased.[19] The observed moment was in fact greater in benzene (3.23 *D*) and in dioxane (3.45 *D*), indicating a mole fraction of the equatorial form which increases to about 0.4 in dioxane.[20] It seemed likely that confirmation of these values could be found in the ultraviolet and infrared spectra, and such was found to be the case (Table I). The increases of the carbonyl stretching frequency were from 3 to 21 cm.$^{-1}$ as the solvent was changed from cyclohexane to dimethyl sulfoxide, which may be compared to +4 cm.$^{-1}$ for an axial and +15 cm.$^{-1}$ for an equatorial halogen in the 2-bromo-4-*t*-butyl-cyclohexanones.[21] Similarly, the shifts of the ultraviolet maxima range from +36 to +21 mμ in cyclohexane and ethanol, compared to about +25 to +20 mμ in the six-membered ring. The extinction coefficients in the ultraviolet are quite large in each case (120 to 180), indicating the presence of a substantial amount of axial form even in the polar solvents.

TABLE I

CARBONYL SHIFTS IN THE INFRARED AND ULTRAVIOLET OF 2-BROMOCYCLOBUTANONE RELATIVE TO CYCLOBUTANONE

Solvent	Infrared $+\Delta_{C=O}$ (cm.$^{-1}$)	$^{+}\Delta\lambda$ (mμ)	$+\Delta$
Cyclohexane	3[a]	36	170
Dioxane	18	20	120
Alcohol[b]	20	21	180
Dimethyl sulfoxide	21	..	..
Neat	20	..	..

[a] Determined at a concentration of about 0.5%; if 10% concentration used, Δ was 13 cm.$^{-1}$. [b] Methanol was used for the infrared measurements, ethanol for the ultraviolet.

A cursory glance was given to the feasibility of calculating the equilibrium point of the ring bending, but using ordinary values for bending and torsional constants[22]; this did not seem possible. The difficulty appeared to be in the fact that the bending constants acceptable for small degrees of angular distortion are poor approximations for an ordinary planar cyclobutane ring, and are useless for predicting how such a structure will further bend.

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(12) (a) N. L. Allinger, *J. Am. Chem. Soc.*, **79**, 3443 (1957); (b) H. van Bekkum, A. VanVeen, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **80**, 1310 (1961).

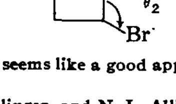
(13) For a compilation of leading references, see N. L. Allinger and H. M. Blatter, *J. Org. Chem.*, **27**, 1523 (1962).

(14) For a chemical and spectroscopic study of the halogenated cyclobutanones in general, see J. M. Conia and J. L. Ripoll, *Bull. Soc. Chim. France*, in press.

(15) R. Arndt, H. H. Günthard and T. Gäumann, *Helv. Chim. Acta*, **41**, 2213 (1958).

(16) The resultant moments calculated here employ as bond noments for C=O and C–Br, 2.76 and 2.24 *D*, except for the equatorial orm where 2.63 and 2.04 *D* were used to allow for induction (ref. 17).

(17) The structure assumed was



θ_1 132.5°
θ_2 113.2°
r_1 1.50 Å.
r_2 1.545 Å.

(18) This seems like a good approximation from the infrared data in Table I.

(19) J. Allinger, and N. L. Allinger *Tetrahedron*, **2**, 64 (1958).

(20) The change in dipole moment with solvent found here is similar to that found in the 2-bromocyclopentanones and 2-bromocyclohexanones (see W. D. Kumler and A. C. Huitric, *J. Am. Chem. Soc.*, **78**, 3369 (1956)).

(21) N. L. Allinger and J. Allinger, *ibid.*, **80**, 5476 (1958).

(22) F. H. Westheimer in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 523.

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PHOTOSENSITIZED *CIS-TRANS* ISOMERIZATION OF THE STILBENES[1]

Sir:

The *cis-trans* isomerization of the stilbenes under the influence of ultraviolet light has been studied by several groups.[2,3,4,5,6] The results are confusing to say the least. The quantum yields for both the *cis-trans* and *trans-cis* processes are close to temperature independent at moderate temperatures but become strongly temperature dependent below about −70°.[3,4] A corresponding temperature effect is observed on the relative yield of fluores-

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(1) Mechanism of Photoreactions in Solution. XII. Part XI is N. J. Turro and G. S. Hammond, *J. Am. Chem. Soc.*, **84**, 2841 (1962).

(2) G. N. Lewis, T. T. Magel and D. Lipkin, *ibid.*, 62 2973 (1940).

(3) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(4) S. Malkin and E. Fischer, "Symposium on Reversible Photochemical Processes," Durham, N. C., April, 1962, symposium papers, p. 281.

(5) D. Schulte-Frohlinde, *ibid.*, p. 295.

(6) H. Stegemeyer, *J. Phys. Chem.*, to be published.

cence from *trans*-stilbene.[3] Furthermore, the composition of the system in the photostationary state depends on the stilbene concentration. As would be anticipated, the photostationary state also depends upon the wave length of the exciting light.[6]

Attempts to explain the results have one common factor, the observation that some activated process must be involved in the interconversion of excited states of the *cis* and *trans* systems. Schulte-Frohlinde[5] suggests that the activated process may be the conversion of excited singlets to a common triplet state having a nonplanar geometric configuration. Stegemeyer[6] prefers to neglect the temperature effect found in the relative yield of fluorescence from *trans*-stilbene and postulates that the excited states of both the *cis* and *trans* systems undergo very efficient intersystem crossing and that the activated process is the interconversion of *cis* and *trans* triplets. On the other hand, Dyck and McClure[3] have observed the $S_0 \rightarrow T_1$ absorption spectrum of *trans*-stilbene in ethyl iodide solution and point out that the presence of a clearly developed vibronic progression having a 1500 cm.$^{-1}$ separation indicates that the central C=C bond retains a substantial amount of double bond character in the lowest (spectroscopic) triplet state. Since there is also a 1600 cm.$^{-1}$ progression in the $S_0 \rightarrow S_1$ absorption spectrum, they conclude that there should be a large barrier to rotation about the central bond in either state.

We have found that the *cis–trans* isomerization can be effected by irradiation of benzene solutions containing either stilbene isomer and photosensitizers. The exciting light is carefully filtered so that unsensitized isomerization can be neglected. The behavior of such a system can be characterized by the composition of the mixture after a photostationary state is established. As is shown in Table I, three sensitizers which have large $S_0 \rightarrow T_1$ excitation energies give the same photostationary states within experimental uncertainty.

TABLE I

Sensitizer	E_T,[7] kcal.	*cis/trans* ratio at photostationary state
Acetophenone	73.9	1.45
Benzophenone	68.7	1.48
Anthraquinone	62.4	1.49

Arguments of the type which have been presented elsewhere[8] suggest strongly that the mechanism of the reaction involves transfer of triplet excitation from excited states of the sensitizers to the stilbenes. Perhaps the most cogent of these arguments is the fact that efficient transfer of singlet excitation is very unlikely because the $S_0 \rightarrow S_1$ transitions of the stilbenes require more energy than is available in a quantum of the light used to excite the sensitizers. Furthermore, since the triplet excitation energies of the sensitizers are larger than those of *cis*- and *trans*-stilbene,[3,9] it is likely that transfer of triplet excitation to either isomer is a diffusion controlled process. Consequently, the composition of the photostationary states should be determined only by the decay process of the stilbene triplets; the composition of the photostationary mixture should be independent of the nature of the sensitizer. The data in Table I indicate that such is the case.

These results seem to show that isomerization of the stilbenes can occur by way of triplet states. They do not *prove* that isomerization under conditions of direct irradiation involves triplet states. Such a hypothesis is made reasonable by consideration of the stationary state obtained upon direct irradiation of stilbenes using the 3130 Å. mercury line. The available results are presented in Table II.

TABLE II

Stilbene concn., m./l.	Solvent	% *cis* at photostationary state	Reference
1×10^{-5}	*n*-Hexane	93	6
4×10^{-5}	Isohexane	93	4
1×10^{-2}	Benzene	92	This work

The figures in Table II are biased by the inequality in the absorption characteristics of the two isomers. At 3130 Å. the ratio of the extinction coefficients of *trans*- to *cis*-stilbene is 7.2.[2] If the excited states involved in the unsensitized isomerization are converted quantitatively to triplets and the latter decay by the ratio observed in the experiments with sensitizers, the predicted *cis/trans* ratio would be $7.2 \times 1.5 = 10.8$ which corresponds to 91.5% *cis*. The agreement with the values in Table II is excellent.

Even if we conclude that *cis-trans* conversion involves triplet states, we need not conclude that there is nearly free rotation in the (spectroscopic) triplet states. These "planar" triplets may be converted to some other, more stable, configuration, or the isomerization may occur in the vibrationally excited S_0 states formed by intersystem crossing from T_1 states.

The behavior of sensitizers having lower $S_0 \rightarrow T_1$ excitation energies is very complex and will be reported later. The variation from behavior of high energy sensitizers is attributed to complications in the energy transfer process.

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OXIDATION-REDUCTION REACTIONS OF COMPLEX AMMINES OF RUTHENIUM(II)-(III)

Sir:

We have been investigating the stoichiometry and rates of reactions involving ammine complexes of Ru(III)-Ru(II). The ions were chosen for study because they differ electronically from complex cobalt ammines in an important way: In the Ru case only d_ϵ electrons come into play in the net

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[7] E_T's refer to 0-0 phosphorescence band in spectra obtained in hydrocarbon glass at 77°K. in these laboratories by Mr. W. G. Herkstroeter.

(8) G. S. Hammond, N. J. Turro and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(9) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).