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 photo-stationary 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 × 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).

change and the comparison of the results with those already obtained for the Co(II)–Co(III) ammines is of significance. Some of the observations made in the current study seem of particular interest and are reported herewith.

In the reduction of $\mathrm{Ru(NH_3)_6^{+++}}$, $\mathrm{Ru(NH_3)_5Cl^{++}}$ or $\mathrm{Ru(NH_3)_5OH_2^{+++}}$ by $\mathrm{Cr^{++}}$, we find that the net changes can be described by the equations

$$\mathrm{Ru(NH_3)_6^{+++} + Cr^{++} \longrightarrow Ru(NH_3)_6^{++} + Cr^{+++}} \tag{1}$$

$$\mathrm{Ru(NH_3)_5Cl^{++} + Cr^{++} \longrightarrow [Ru(NH_3)_5^{++}]^{1} + CrCl^{++}} \tag{2}$$

$$\mathrm{Ru(NH_3)_5OH_2^{+++} + Cr^{++} \longrightarrow Ru(NH_3)_5^{++} + Cr^{+++}} \tag{3}$$

The 1:1 stoichiometry has been established in reactions (1) and (2) with an accuracy of at least 10%. The Ru containing products of the reduction of $\mathrm{Ru(NH_3)_5Cl^{++}}$ and $\mathrm{Ru(NH_3)_5OH_2^{+++}}$ by $\mathrm{Cr^{++}}$ appear to be identical. Both reactions produce a substance having $\epsilon = 260\ M^{-1}$ cm.$^{-1}$ at 327.5 mμ (not a maximum for Ru(II) but a maximum for $\mathrm{Ru(NH_3)_5Cl^{++}}$), and having a weak absorption maximum at 420 mμ ($\epsilon \sim 10^2$). The Cr containing product of reaction 1 has been identified as $\mathrm{Cr(H_2O)_6^{+++}}$, and $\mathrm{CrCl^{++}}$ has been shown to comprise at least 90% of the Cr product in reaction 2.

By reoxidizing the Ru(II) species, it has been shown that the Ru(II)–$\mathrm{NH_3}$ bonds remain intact in acidic solution (up to 0.2 M) for at least one hour. A convenient oxidizing agent has proved to be $\mathrm{ClO_4^-}$. Rate studies were made of the reaction of $\mathrm{Ru(NH_3)_5^{++}}$ with $\mathrm{ClO_4^-}$ at 25° using a medium ($\mathrm{Na^+}$, $\mathrm{H^+}$, $\mathrm{Cl^-}$, $\mathrm{ClO_4^-}$) at $\mu = 0.14$. The reaction is first order in $\mathrm{Ru(NH_3)_5^{++}}$ and $\mathrm{ClO_4^-}$ and zero order in $\mathrm{H^+}$ at least in the range from 10^{-3} to 10^{-2} M, and the specific rate is $26 \pm 1 \times 10^{-3}$ M^{-1} sec.$^{-1}$. When $\mathrm{Ru(NH_3)_6^{++}}$ is the reactant the reaction is slower by a factor of about 50.

The half-life for the aquation of $\mathrm{Ru(NH_3)_5Cl^{++}}$ is greater than 10^5 sec., but when $\mathrm{Ru(NH_3)_5^{++}}$ is present, the reaction may be complete in a few minutes. $\mathrm{Ru(NH_3)_5^{++}}$ is very efficient in bringing into equilibrium a number of reactions of the type

$$\mathrm{Ru(NH_3)_5OH_2^{+++} + X = Ru(NH_3)_5^{III}X + H_2O}$$

Making use of this catalytic effect, the equilibrium quotient in the reaction with $\mathrm{X = Cl^-}$ has been determined as 43 ± 3 at 25° and $\mu = 0.1$. The reactions which bring about the equilibration are

$$\mathrm{Ru(NH_3)_5OH_2^{+++} + Ru(NH_3)_5^{++} + Cl^- \longrightarrow} \tag{4}$$

$$\mathrm{Ru(NH_3)_5Cl^{++} + Ru(NH_3)_5^{++} \longrightarrow} \tag{5}$$

and the specific rates have been determined approximately as $4 \times 10^3\ M^{-2}$ sec.$^{-1}$ and 2×10^2 M^{-1} sec.$^{-1}$. The ratio agrees within experimental error with the value which was measured for the equilibrium quotient. Substitution on $\mathrm{Ru(NH_3)_5^{++}}$ apparently is not rate determining for the catalysis under our conditions, and taking into account the concentration levels of the reagents, we conclude that for substitution on $\mathrm{Ru(NH_3)_5^{++}}$, $t_{1/2} < 10$ sec.

The specific rates of reactions 1 and 2 are *ca.* $1 \times 10^2\ M^{-1}$ sec.$^{-1}$ and $8 \times 10^3\ M^{-1}$ sec.$^{-1}$. The rate of reaction 1 is very sensitive to $\mathrm{Cl^-}$, and the sensitivity appears to be about the same as it is for the reaction of $\mathrm{Cr^{++}}$ with $\mathrm{Co(NH_3)_6^{+++}}$.[2]

Experimental.—$\mathrm{Ru(NH_3)_6Cl_3}$ was supplied by Johnson–Matthey & Co., London. $\mathrm{Ru(NH_3)_5Cl_3}$ was prepared by heating $\mathrm{Ru(NH_3)_6Cl_3}$ with concentrated hydrochloric acid.[3] $\mathrm{Ru(NH_3)_5OH_2(ClO_4)_3}$ was prepared from $\mathrm{Ru(NH_3)_5Cl_3}$ by dissolving in $\mathrm{NH_3}$ aq. then acidifying with concentrated $\mathrm{HClO_4}$. Ru was analyzed spectrophotometrically by the method of Woodhead and Fletcher[4] and using the characteristic absorptions of the various Ru(III) ammine species.[5] We have found ϵ for $\mathrm{Ru(NH_3)_5OH_2^{+++}}$ to be 757 M^{-1} cm.$^{-1}$ at the absorption maximum, $\lambda = 268$ mμ.

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[1] This species is almost certainly $\mathrm{Ru(NH_3)_5OH_2^{++}}$, but experimental proof that it actually is hexacoördinated is lacking.

[2] A. M. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).

[3] K. Gleu and K. Rehm, *Z. anorg. Chem.*, **227**, 237 (1936).

[4] J. L. Woodhead and J. M. Fletcher, *J. Chem. Soc.*, 5039 (1961).

[5] H. Hartmann and C. Buschbeck, *Z. physik. Chem.*, **11**, 120 (1957).

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RECEIVED NOVEMBER 15, 1962

STERIC COURSE OF SOME CARBENOID ADDITIONS TO OLEFINS[1]

Sir:

Additions of unsymmetrically substituted carbenoid intermediates to olefins lacking a center of symmetry result in pairs of isomeric cyclopropanes. With the exception of carboethoxycarbene additions,[2] no proof of the configurations of the products has been given. For a number of cases, however, it has been *assumed* that steric hindrance in the transition state will be product controlling, and, being similar to that in the products, will lead to the predominance of the isomer with the fewest nonbonded interactions.[3a–c] We wish to present evidence that this assumption is not generally valid and that the previously assumed configurations of some chlorocyclopropanes are in error.[3a]

Treatment of benzal bromides I–III with alkyllithiums in the presence of olefins gave arylcyclopropanes in moderate yields. The same compounds also were obtained from photolysis of the corresponding aryldiazomethanes using olefins as solvents. With 1-butene (IV), *cis*-2-butene (V) and 2-methyl-2-butene (VI) as substrates the expected isomers were formed in ratios as listed in the table.

Assignment of configurations by n.m.r. and independent syntheses show that the predominantly formed isomers have the configuration in which the larger number of alkyl groups and the aryl sub-

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[1] This work was supported by a grant from The Petroleum Research Fund, administered by The American Chemical Society.

[2] W. v. E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960); P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961).

[3] (a) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960); (b) E. E. Schweizer and W. E. Parham, *ibid.*, **82**, 4085 (1960); (c) U. Schöllkopf and G. J. Lehmann, *Tetrahedron Letters*, **4**, 165 (1962).