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

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

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

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

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 $Ru(NH_3)_5Cl^{++}$ and $Ru(NH_3)_5OH_2^{+++}$ by 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 $Ru(NH_3)_5Cl^{++}$), and having a weak absorption maximum at 420 mμ ($\epsilon \sim 10^2$). The Cr containing product of reaction 1 has been identified as $Cr(H_2O)_6^{+++}$, and $CrCl^{++}$ 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)–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 ClO_4^-. Rate studies were made of the reaction of $Ru(NH_3)_5^{++}$ with ClO_4^- at 25° using a medium (Na^+, H^+, Cl^-, ClO_4^-) at $\mu = 0.14$. The reaction is first order in $Ru(NH_3)_5^{++}$ and ClO_4^- and zero order in 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 $Ru(NH_3)_6^{++}$ is the reactant the reaction is slower by a factor of about 50.

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

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

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

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

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

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 $Ru(NH_3)_5^{++}$ 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 $Ru(NH_3)_5^{++}$, $t_{1/2} < 10$ 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 Cl^-, and the sensitivity appears to be about the same as it is for the reaction of Cr^{++} with $Co(NH_3)_6^{+++}$.[2]

Experimental.—$Ru(NH_3)_6Cl_3$ was supplied by Johnson-Matthey & Co., London. $Ru(NH_3)_5Cl_3$ was prepared by heating $Ru(NH_3)_6Cl_3$ with concentrated hydrochloric acid.[3] $Ru(NH_3)_5OH_2(ClO_4)_3$ was prepared from $Ru(NH_3)_5Cl_3$ by dissolving in NH_3 aq. then acidifying with concentrated $HClO_4$. 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 $Ru(NH_3)_5OH_2^{+++}$ to be 757 M^{-1} cm.$^{-1}$ at the absorption maximum, $\lambda = 268$ mμ.

Acknowledgment.—This work was supported by the National Science Foundation under Grant G-20954. The spectrophotometer used was purchased under Grant G-22611 from the National Science Foundation.

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[1] This species is almost certainly $Ru(NH_3)_5OH_2^{++}$, 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).

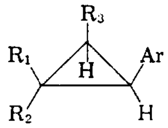
(3) (a) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960); (b) E. E. Schweizer and W. E. Parham, *ibid.*, **82**, 4085 (1960); (c) U. Schöllkopf and G. J. Lehmann, *Tetrahedron Letters*, **4**, 165 (1962).

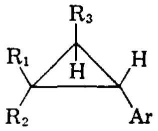
stituent are located on the same side of the ring (subsequently referred to as the *cis* configuration).

Chemical shifts of the alkyl proton resonances of adducts VII (both methylene and methyl protons) and VIII and of two methyl groups of adducts IX are 0.18 to 0.45 p.p.m. higher in the predominant isomers than the corresponding resonances of the minor adducts. Deriving geometrical parameters from scale models, it can be shown that the *cis* oriented alkyl groups are located in the diamagnetic shielding cone of the aryl ring[4] in or near those conformations of the aryl substituent which can be expected to be the most stable. In contrast the *trans* alkyl substituents find themselves in the paramagnetic zone in any conformation. Similarly, the observed larger shielding of the benzylic ring protons of the minor adducts are in line with expectations considering the diamagnetic effect of the *cis* oriented ring alkyl carbon carbon bonds.[5] Further support for this assignment is found in the larger spin-spin couplings of the vicinal ring protons with the benzylic protons in the predominant isomers. The stronger coupling has been demonstrated to be associated with *cis* orientation in a number of cyclopropanes with known configurations.[6] Finally, independent syntheses of the minor adducts to IV from *trans*-1-aryl-1-butenes *via* the stereospecific Simmons–Smith reaction[7] render the assignments of configurations unambiguous.

$X{-}C_6H_4{-}CHBr_2$

I, X = H, II, X = CH_3, III, X = Cl





VIIa, $R_1 = C_2H_5$, $R_2 = R_3 = H$
VIIIa, $R_1 = R_3 = CH_3$, $R_2 = H$
IXa, $R_1 = R_2 = R_3 = CH_3$
VIIb, $R_1 = C_2H_5$, $R_2 = R_3 = H$
VIIIb, $R_1 = R_3 = CH_3$, $R_2 = H$
IXb, $R_1 = R_2 = R_3 = CH_3$

ISOMER RATIOS AS OBTAINED FROM BENZAL BROMIDES[a] AND PHOTOLYSIS OF ARYLDIAZOMETHANES (IN PARENTHESES) WITH OLEFINS IV, V AND VI[b]

	Ar = C_6H_5	Ar = p-CH_3-C_6H_4	Ar = p-Cl-C_6H_4
VIIa/VIIb	2.1 (1.0)	2.8 (1.3)	2.1 (1.1)
VIIIa/VIIIb	2.4 (1.1)	4.5 (1.4)	3.4 (1.2)
IXa/IXb	1.3 (1.1)	1.4 (1.3)	1.4 (1.1)

[a] *n*-Pentane used as solvent. [b] Reaction temperature in both series, −10°.

The above mentioned correlations of relative magnitudes of vicinal proton spin spin coupling and of chemical shifts of ring protons with configurations[8] on three membered rings made it very probable that the previous assignments of configurations to some chlorocyclopropanes, obtained from additions of chlorocarbene to olefins, are in error.[3a] We have now synthesized the two adducts of chlorocarbene to 1-butene from *cis* and *trans* 1-chloro-1-butene *via* the Simmons–Smith reaction.[7] Identity of the product obtained from *trans*-1-chloro-1-butene with the minor adduct of the carbene reaction and *vice versa* established that here again the major product of chlorocarbene addition has the *cis* orientation and that the original assignments should be reversed.

A possible explanation of the observed stereochemistry may be found in the assumption of a transition state with considerable charge separation.[9] Partial delocalization of opposite charges over the alkyl groups by hyperconjugative effects and over the aryl and chlorine substituent, respectively, by inductive effects, will lead to smaller over-all charge separation in the *cis* transition state. Observed solvent dependence, leading to smaller ratios in more polar solvents, such as ether, concur with this explanation.[10] The striking similarity of the steric course of these carbene additions with the Diels-Alder reaction should be pointed out, and, perhaps, may be regarded to be more than just a coincidence.[11]

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[4] Determined according to C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[5] J. I. Musher, *ibid.*, **35**, 1159 (1961), and private communication.

[6] J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962), and references cited therein.

[7] H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

[8] The predominantly formed adducts of chlorocarbene to IV, V and VI show larger vicinal spin spin coupling and decreased shielding of the proton located on the carbon bearing the chlorine atom.[3a]

[9] This assumption is strongly supported by the established electrophilic nature of carbenoid intermediates: W. v. E. Doering and W. A. Henderson, *J. Am. Chem. Soc.* **80**, 5274 (1958); G. L. Closs and G. M. Schwartz, *ibid.*, **82**, 5729 (1960).

[10] Naturally, other factors, such as the degree of bond formation in the transition state, determined in part by the ground state stability of the carbenoid intermediate will influence the magnitude of the isomer ratio as well. The small but experimentally significant preference for the formation of same isomer in the diazo compound photolysis indicates that the probable incorporation of a molecule of lithium halide in the transition state of the α-elimination reaction is not the sole factor in determining the stereochemistry.

[11] Satisfactory analyses have been obtained for all new compounds.

[12] A. P. Sloan Foundation Fellow, 1962-1964.

[13] National Science Foundation Predoctoral Coöperative Fellow, 1961-1963.

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RECEIVED SEPTEMBER 5, 1962

ON THE COPOLYMERIZATION OF BENZENE

Sir:

Considerable interest was generated by claims that benzene copolymerizes with vinyl acetate,[1] methyl methacrylate,[2] and styrene.[3] More recently, however, the vinyl acetate work has been refuted[4] and the styrene claim withdrawn.[5] Both sets of workers[4,5] found radioactive impurities in their benzene which led to erroneous results. Although the matter seems settled for these two monomers, the question of whether copolymeriza-

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[1] W. H. Stockmayer and L. H. Peebles, *J. Am. Chem. Soc.*, **75**, 2278 (1953); L. H. Peebles, Jr., J. T. Clarke and W. H. Stockmayer, *ibid.*, **82**, 4780 (1960).

[2] D. B. Anderson, G. M. Burnett and A. C. Gowan, IUPAC Symposium on Macromolecular Chemistry, Moscow, 1960, Sec. II, p. 111.

[3] G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **48**, 237 (1961).

[4] J. W. Breitenbach, G. Billek, G. Falthansl and E. Weber, *Monatsh. Chem.*, **92**, 1100 (1961).

[5] G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **51**, 236 (1962).