

major product. Our work is continuing in order to define the scope of this reaction, and to assess the implications for the mechanisms of other radiation-induced reactions in organic media.

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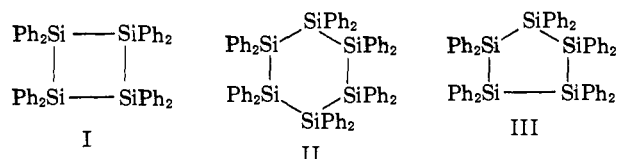
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DECAPHENYLCYCLOPENTASILANE

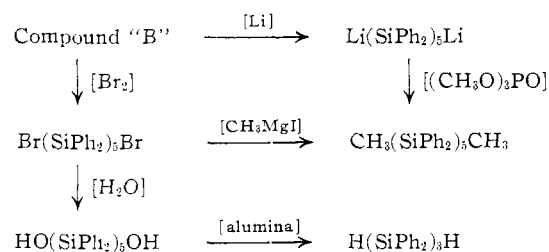
Sir:

The reaction of dichlorodiphenylsilane with sodium^{1,2} or lithium^{2b,3} produces several perphenylated cyclosilanes. One of them, designated Compound "B" by Kipping,^{1a} was first proposed to be octaphenylcyclo-tetrasilane (I)^{1a,b}; and, more recently, to be dodeca-phenylcyclohexasilane (II).³ Both of these proposals were based on molecular weight determinations; the



former on values determined cryoscopically in benzene and camphor^{1a,b} and the latter on values determined cryoscopically in perylene.³ It now has been shown that both proposals were in error and that Compound "B" is decaphenylcyclopentasilane (III). Derivatives of this compound, which had previously been designated as hexasilanes,^{3,4} are in fact 1,5-disubstituted-decaphenylpentasilanes.

Chemical proof for the structure of decaphenylcyclopentasilane has been obtained by two different means starting with decaphenylcyclopentasilane. In a recent publication,⁵ it has been shown that the α,ω -dihydroxy derivative of Compound "B" (decaphenylcyclopentasilane), when chromatographed on basic alumina, provides 1,1,2,2,3,3-hexaphenyltrisilane. This reaction indicates that the dihydroxy compound was a pentasilane and that Compound "B" is the cyclopentasilane.



The lithium cleavage products of Compound "B" were examined to throw more light on the structure of the cyclic polysilane. It was found that when the cyclosilane was allowed to react with lithium in tetrahydrofuran for 2 hr., the cleavage was essentially com-

(1) (a) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830 (1921); (b) F. S. Kipping, *ibid.*, **123**, 2590 (1923); (c) **125**, 2291 (1924); (d) 2719 (1927).

(2) (a) H. Gilman, D. J. Peterson, A. W. Jarvie and H. J. S. Winkler, *J. Am. Chem. Soc.*, **82**, 2076 (1960); (b) A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson and H. Gilman, *ibid.*, **83**, 1921 (1961).

(3) (a) H. Gilman, D. J. Peterson, A. W. Jarvie and H. J. S. Winkler, *Tetrahedron Letters*, **23**, 5 (1960); (b) H. J. S. Winkler, A. W. P. Jarvie, D. J. Peterson and H. Gilman, *J. Am. Chem. Soc.*, **83**, 4089 (1961).

(4) (a) A. W. P. Jarvie and H. Gilman, *Chem. Ind. (London)*, 1271 (1960); (b) A. W. P. Jarvie, H. J. S. Winkler and H. Gilman, *J. Org. Chem.*, **27**, 614 (1962); (c) H. J. S. Winkler and H. Gilman, *ibid.*, **27**, 254 (1962).

(5) G. R. Chainani, S. Cooper and H. Gilman, *ibid.*, in press.

plete. Formation of derivatives, using trimethyl or tri-*n*-butyl phosphate⁶ or chlorotrimethylsilane, led to derivatives of the corresponding 1,5-disubstituted compounds, in yields approaching 83%. The constitutions of these compounds were established by elemental analysis and by proton magnetic resonance spectra determinations to obtain aliphatic to aromatic hydrogen atom ratios. 1,5-Dimethyldecaphenylpentasilane was also obtained in high yield from the reaction of methylmagnesium iodide with 1,5-dibromodecaphenylpentasilane.

Molecular weight determinations have been obtained for decaphenylcyclopentasilane (molecular weight 911) by three different methods which gave consistent results. Ebullioscopic determinations in toluene⁷ using octaphenylcyclo-tetrasilane as a standard gave a value of 921 ± 7 (four determinations). An X-ray diffraction study and density determination of decaphenylcyclopentasilane, crystallized from benzene-ethanol, provided a value of 983, in good agreement with a value of 989 calculated for decaphenylcyclopentasilane plus one molecule of benzene, which was subsequently shown to be present. The molecular weight was also determined in benzene using a "vapor phase osmometer"⁸ at several concentrations. Extrapolation to zero concentration gave a value of 912, in excellent agreement with the theoretical value of 911 for decaphenylcyclopentasilane.

Experimental details for the reactions and data presented here and for other polysilanes derived from decaphenylcyclopentasilane will be forthcoming.

Acknowledgments.—The authors wish to express their gratitude to Drs. C. A. Glover, H. W. Patton and W. D. Kennedy, of the Tennessee Eastman Co., for the ebullioscopic and X-ray determinations. This research was supported in part by the United States Air Force under Contract AF 33(616)-6463 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

(6) H. Gilman and B. J. Gaj, *ibid.*, **26**, 247 (1961).

(7) C. A. Glover and R. R. Stanley, *Anal. Chem.*, **33**, 447 (1961).

(8) Mechrolab, Inc., Mountain View, Calif.

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THE REDUCTIONS OF *cis*- AND *trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ AND $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$ BY Fe^{++}

Sir:

We have measured spectrophotometrically the rates of reduction of *cis*- and *trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ and $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$ by Fe^{++} in aqueous perchlorate solutions (no other anions present) at 25°. The results, summarized in Table I, show that the reduction of the *cis* complex is acid-independent for (H^+) varying from 0.072 to 0.219 *M*, whereas that of the *trans* complex is, under the same conditions, strongly acid-dependent. The rate laws (time in minutes) are given by the equations $11.1(\text{Fe}^{++})$ (*cis*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$) and $[4.4 + 82(\text{H}^+)](\text{Fe}^{++})$ (*trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$). The reduction of $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$ is acid-independent and obeys the rate law $0.52(\text{Fe}^{++})(\text{Co}(\text{NH}_3)_5\text{N}_3^{++})$.

Because of the substitution-lability of $\text{Fe}(\text{III})$, it cannot be ascertained whether these reactions proceed *via* a bridged or outer-sphere activated complex.¹ However, assuming that bridged activated complexes are operative, reasonable explanations can be advanced for the present observations.

(1) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

TABLE I

THE REACTIONS OF *cis*- AND *trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ AND $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$ WITH Fe^{++} AT 25° , $\Sigma(\text{ClO}_4^-) = 0.26$

Complex	$\times 10^5, M$	$(\text{Fe}^{++}), M$	$(\text{H}^+), M$	$k^{a,b}, \text{min.}^{-1}$	$k_2^c, M^{-1} \text{min.}^{-1}$
<i>cis</i>	11.8	0.0185	0.072	0.203	11.0
<i>cis</i>	11.8	.0185	.131	.200	10.8
<i>cis</i>	11.8	.0185	.189	.207	11.2
<i>cis</i>	7.41	.0185	.219	.210	11.3
<i>cis</i>	11.8	.0093	.183	.108	11.6
<i>cis</i>	11.8	.0370	.144	.401	10.8
<i>trans</i>	3.87	.0185	.072	0.190, 0.193	.190 ^d
<i>trans</i>	3.87	.0185	.131	0.280	.281 ^d
<i>trans</i>	3.87	.0185	.189	.380	.369 ^d
<i>trans</i>	3.87	.0185	.219	0.416, 0.411	.414 ^d
<i>trans</i>	3.87	.0093	.219	0.206	.207 ^d
<i>trans</i>	3.87	.0370	.144	.594	.600 ^d
---	155°	.148	.58	.077	.52 ^f
---	78°	.074	.29	.0392	.53 ^f

^a Pseudo first-order rate constant obtained from the slope of $\log(D_t - D_\infty)$ vs. time. ^b Corrected for the acid-catalyzed aquation⁷ of $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$. Correction amounts to 2-6% except for experiment 5, where it is 10%. ^c Second-order rate constant $k_2 = k/(\text{Fe}^{++})$. ^d Calculated using the expression $[4.4 + 82(\text{H}^+)]/(\text{Fe}^{++})$. ^e The reactant is $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$. ^f $\Sigma(\text{ClO}_4^-) = 0.89$.

The observed reactivity order toward reaction with Fe^{++} , *cis*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+ > \text{trans}-\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+ \gg \text{Co}(\text{NH}_3)_5\text{N}_3^{++}$, cannot be explained invoking solely the effect of ligands *trans* to the bridging group²: according to the *trans* effect, one would expect *cis*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ to react at approximately the same rate as $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$.³ Alternately, it could be assumed that replacement of one NH_3 in $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$ by N_3^- , whether in the *cis* or *trans* positions, results in an increased rate of reaction with Fe^{++} , perhaps by stabilization of the Co orbital which accepts the electron.^{2,4} However, in view of the efficiency of the acid-catalyzed path for the reaction of *trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ with Fe^{++} , it becomes difficult to understand why acid-catalysis is not observed for the *cis* isomer.

We suggest, therefore, that the reaction of *cis*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ with Fe^{++} proceeds *via* a double-bridged activated complex entirely analogous to the one recently demonstrated for the reaction between $\text{Cr}(\text{N}_3)_2^+$ and Cr^{++} .⁵ This interpretation receives further support when the ratio of the rate constants for the reactions of *cis*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ and $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$ with Fe^{++} is compared with the corresponding ratio for the reactions of *cis*- $\text{Cr}(\text{N}_3)_2^+$ and CrN_3^{++} with Cr^{++} . The observed ratio for the Co(III) complexes is approximately 20, and, when corrected for the difference in ionic strengths,⁶ this ratio will be close to the value of 50 observed⁵ for the chromium system.

The increased reactivity of *trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ as compared to $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$ is consistent with a *trans*-effect in electron-transfer reactions,² and the observed acid-catalysis further supports this interpretation: the N_3^- *trans* to the bridging N_3^- has a site available for a proton attachment, and movement of the

trans N_3^- away from the Co center as electron transfer occurs¹ is facilitated by protonation.⁷

Acid-catalyzed paths for electron-transfer reactions between metal ions, although not unprecedented, are not a common occurrence. Such paths have been observed previously in systems where addition of a proton improves the conjugation of two metal centers connected by an unsaturated bridging ligand,¹ and for the reactions of carboxylatotetraamminecobalt(III) complexes with Cr^{++} .⁴

(7) Facilitation of the removal of N_3^- by protonation has been observed in other systems (A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 583 (1962)) and is further supported by unpublished experiments showing that the aquations of *cis*- and *trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ between 0.2 and 1.2 M H^+ are first order in complex and first order in H^+ , with undetectable contributions of H^+ -independent paths.

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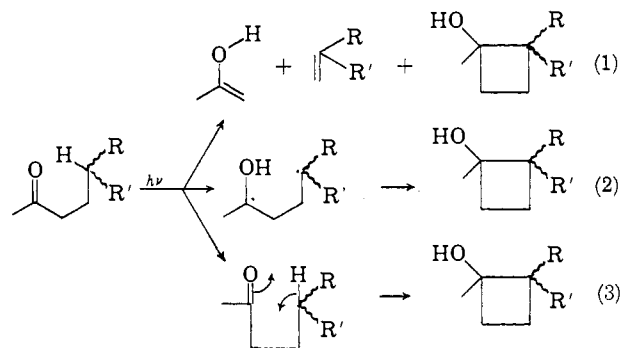
ALBERT HAIM

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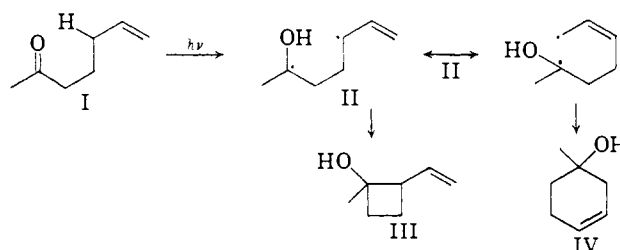
ON THE MECHANISM OF PHOTOCHEMICAL FORMATION OF CYCLOBUTANOLS

Sir:

Aliphatic ketones containing γ -hydrogen upon irradiation with ultraviolet light in solution undergoes two concurrent reactions, the type II cleavage¹ and the formation of cyclobutanols.² Both reactions appear to be intramolecular with little or no detectable side reactions.³ In the cases of 2-octanone and 20-ketosteroids, two isomeric cyclobutanols are obtained.⁴ Two mechanisms have been proposed for the photochemical formation of cyclobutanols, one a step-wise mechanism² (eq. 2) and the other a concerted mechanism⁵ (eq. 3). On the basis of available experimental data, these two mechanisms cannot be differentiated.



The irradiation of 6-hepten-2-one [I] was undertaken in order to provide direct evidence as to the mechanism of the cyclobutanol formation. Should the reaction proceed by a concerted mechanism, the products would contain only cyclobutanols. However, if the intermediate is a free radical, an allyl radical [II] in this



(1) R. G. W. Norrish, *Trans. Faraday Soc.*, **33**, 1521 (1937).

(2) N. C. Yang and D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

(3) W. Davis, Jr., and W. A. Noyes, Jr., *ibid.*, **69**, 2153 (1947); P. Ausloos and R. E. Rebert, *ibid.*, **83**, 4897 (1961).

(4) N. C. Yang and D. H. Yang, *Tetrahedron Letters*, **4**, 10 (1960); O. Jeger, *et al.*, *Helv. Chim. Acta*, **43**, 354 (1960).

(5) O. Jeger, *et al.*, *ibid.*, **42**, 2122 (1959).

(2) L. Orgel, Report of the Tenth Solvay Conference, Brussels, 1956, p. 289.

(3) It is not likely that the increased reactivity of the *cis* complex as compared to $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$ is a consequence of the decrease in charge. Thus, CrF^{--} reacts with Cr^{++} at a faster rate than *cis*- or *trans*- CrF_2^+ (Y. T. Chia and E. L. King, *Discussions Faraday Soc.*, **29**, 109 (1960)). Furthermore, an equilibrium mixture of *cis*- and *trans*- $\text{Co}(\text{NH}_3)_4\text{OH}_2\text{N}_3^{++}$ reacts with Fe^{++} in 1.2 M HClO_4 70 times faster than $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$ (A. Haim, unpublished results). See also ref. 4.

(4) K. D. Kopple and R. R. Miller, *Proc. Chem. Soc.*, 306 (1962).

(5) R. Snellgrove and E. L. King, *J. Am. Chem. Soc.*, **84**, 4610 (1962).

(6) The reactions of *cis*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ and $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$ were studied at $\Sigma(\text{ClO}_4^-)$ values of 0.26 and 0.89, respectively.