Isopropyl acrylate-α,β-d_2 with $\gamma = 6$ and isopropyl acrylate-β-d_1 with $\gamma = {}^1/_6$ were prepared as described previously.[3] Isopropyl acrylate-*trans*-β-d_1 was prepared by reduction of isopropyl propiolate-β-d_1 in H_2O according to the method of Botti and Furman.[10] Preparation and purification of the oligomers were performed by the method described previously.[1,3] The nmr spectra were measured on pure liquids by a Varian HR-100 spectrometer at room temperature.

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Rapid Rearrangements in the *t*-Amyl Cation and the Relative Sign of the Coupling Constants

Sir:

Rearrangements of carbonium ions have long been postulated to explain numerous reactions in organic chemistry. Recently, it has been possible to observe these reactions directly through nmr spectroscopy of several stable carbonium ions.[1,2] We report here a study of the temperature-dependent nmr spectrum of *t*-amyl cation which yields information about the rearrangement mechanism and also the relative signs of the two coupling constants visible in the spectrum.

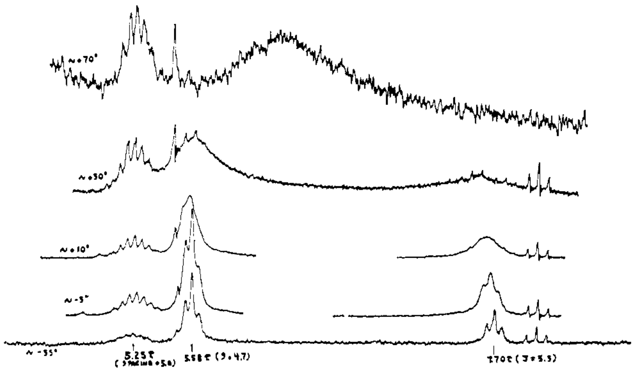
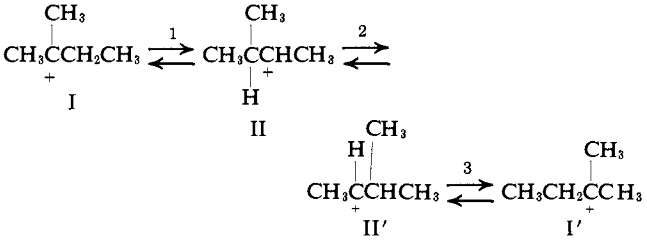


Figure 1.

We prepared *t*-amyl cation by allowing 2-chloro-2-methylbutane to react with excess antimony pentafluoride in sulfuryl chlorofluoride in a vacuum line at −90° with stirring. Below −40° its nmr spectrum, taken in a coaxial cell to provide a standard peak, was very similar to that previously reported,[3,4] with impurity peaks at the position of *t*-butyl cation and at high field (Figure 1). Up to 140° the spectrum showed only continuation of the changes visible in Figure 1, the methylene multiplet remaining unchanged at higher temperatures. Upon recooling the sample, the original spectrum was reobtained. The spectral changes demonstrate interchange of the two types of methyl without mixing in the CH_2 hydrogens.

We have accounted for the temperature dependence of the nmr spectrum as shown.



$$\underset{\text{I}}{CH_3\overset{CH_3}{\underset{+}{C}}CH_2CH_3} \overset{1}{\rightleftarrows} \underset{\text{II}}{CH_3\overset{CH_3}{\underset{H}{C}}\overset{}{\underset{+}{C}}HCH_3} \overset{2}{\rightleftarrows} \underset{\text{II}'}{CH_3\overset{H}{\underset{+}{C}}\overset{CH_3}{C}HCH_3} \overset{3}{\rightleftarrows} \underset{\text{I}'}{CH_3CH_2\overset{CH_3}{\underset{+}{C}}CH_3}$$

All other simple rearrangements of *t*-amyl cation give primary carbonium ions and are therefore considered less likely. Furthermore, mechanisms involving primary ions could easily completely mix all types of hydrogen. Step 2 is analogous to the 1–2 rearrangement in pentamethylethyl cation. Nmr line-shape and spin-echo methods have so far yielded only a lower limit for this rate, of ~5000 sec^{-1} at −180°.[4] Nevertheless, we feel that step 2 is rate determining, since hydride shifts are generally more rapid than analogous methide shifts.

Both unimolecular and bimolecular processes have been proposed in the rearrangement of 2-chloro-2-methylbutane[5,6] induced by aluminum chloride. However, dimer formation followed by rearrangement and cleavage can be ruled out in our case, since interchange of either methyl or methylene hydrogens between molecules would be expected. The unchanged fine structure in the methylene multiplet at high temperature is inconsistent with rapid intermolecular exchange of hydrogen.

A careful consideration of the origin of the various lines of this multiplet leads to the conclusion that, were the two separate coupling constants of this methylene to the adjacent methyl and to the downfield methyl opposite in sign, interchange of methyls would collapse this fine structure. Since this does not occur, we conclude that the signs of these coupling constants (through three and four bonds) are identical. This method of using a fast reaction to determine relative signs of coupling constants has not been previously reported.

Theoretical curves for the spectrum as a function of rate were calculated using the general many-site computer program previously described.[1,2,7] The small temperature dependence observed here of the chemical shift below −30° was extrapolated to give the shifts which were used. The observed nmr spectrum of the upfield triplet at −20.0° was recorded digitally on magnetic tape. Convolution with this curve in the computer introduced both the natural line shape in the absence of exchange and the triplet structure, and made it possible to determine accurate rate constants using the low-temperature spectra. The use of the usual Lorentzian line shapes led to points off the Arrhenius line. At different temperatures either the peak intensity ratios, the widths of the coalesced multiplets, or the frequency of maximum intensity of the broad single line of the experimental spectra was compared with similar features

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(1) M. Saunders, G. Olah, and P. Schleyer, *J. Am. Chem. Soc.*, **86**, 5680 (1964).

(2) M. Saunders in "Magnetic Resonance in Biological Systems," A. Ehrenberg, Ed., Pergamon Press, Ltd., Oxford, 1967, pp 85–99.

(3) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastein, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

(4) G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967).

(5) G. J. Karabatsos and F. M. Vane, *ibid.*, **85**, 729 (1963).

(6) G. J. Karabatsos, F. M. Vane, and S. Meyerson, *ibid.*, **85**, 733 (1963).

(7) M. Saunders, *Tetrahedron Letters*, 1699 (1963).

of the calculated spectra to obtain the rates. At some temperatures visual comparison was found most effective in obtaining the rates. Rate constants (using the natural line shape) are shown in Table I.

Table I

Temp, °C	k, sec^{-1}	Method
−15.8	1.20	Maximum-minimum ratios
−10.0	2.45	Maximum-minimum ratios
−7.3	3.75	Maximum-minimum ratios
−0.9	6.95	Maximum-minimum ratios
+0.2	8.50	Maximum-minimum ratios
2.0	10	Visual comparison
5.5	13	Visual comparison
8.0	17	Visual comparison
12.3	34.2	Half-height width
19.5	54.7	Half-height width
23.0	79.0	Half-height width
30.0	132	Half-height width
49.0	550	Visual comparison
58.0	990	Chemical shift

A least-mean-square Arrhenius fit made by computer gave $E_A = 15.3 \pm 0.2$ kcal/mole and $\log A = 13.2 \pm 0.2$,[8] where the errors quoted are standard deviations. The rate constants at 5, 13, and 55° for the *t*-amyl cation made from *t*-amyl alcohol with fluorosulfonic acid and antimony pentafluoride in sulfuryl chlorofluoride lay close to or on the best Arrhenius line through the data in Table I.

A further comment on the significance of the activation energy measured in this work is necessary. If, as has been suggested, the methide shift in step 2 is rate determining, then what has been measured is the sum of the energy difference between the secondary and tertiary ions and the activation energy for this methide shift. Since the activation energy for this methide shift, which is analogous to that in the pentamethylethyl cation, is probably less than 4 kcal, the tertiary–secondary ion enthalpy difference should then be 11–15 kcal/mole.

Acknowledgment. We wish to acknowledge support of this work by the National Science Foundation.

[8] D. M. Brouwer, *et al.*, report $E_A = 14.3$ kcal/mole and $\log A = 12.7$, but gave no details: D. M. Brouwer and E. L. Mackor, *Proc. Chem. Soc.*, 147 (1964).

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Photosynthesis of Some Werner Complexes of Rhodium(III) and Iridium(III)

Sir:

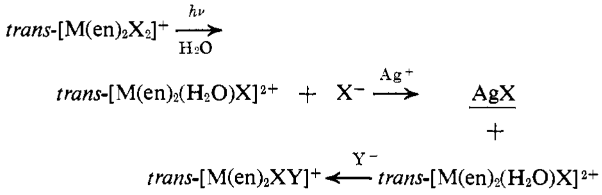
Although much work has been done recently in elucidating mechanisms and products of inorganic photochemical reactions of metal complexes,[1] these reactions have not been used in the synthesis of Werner complexes. We wish to report a useful photochemical route for the preparation of mixed diacidobis(ethylenediamine) complexes of the type *trans*-$[M(en)_2XY]^{n+}$ (M = Rh(III), Ir(III)).

In contrast to the photochemistry of Co(III),[2] the photochemical substitutions of complexes of its congeners Rh(III) and Ir(III) are not complicated by reduction of the central metal atom, nor do *trans* → *cis* isomerizations occur in the complexes studied.

The compounds *trans*-$[M(en)_2X_2]^+$ (M = Rh(III), Ir(III); X = Cl, Br, I) in aqueous solution undergo rapid photosubstitutions to yield *trans*-$[M(en)_2(H_2O)X]^{2+}$. The reactions are characterized by nearly quantitative yields and, where they exist during reaction, excellent isosbestic points in their ultraviolet absorption spectra are observed (Figure 1). In the presence of excess Br^- and I^-, *trans*-$[Ir(en)_2Cl_2]^+$ reacts photochemically in aqueous solution at 25° to give *trans*-$[Ir(en)_2Br_2]^+$ and *trans*-$[Ir(en)_2I_2]^+$, respectively. *trans*-$[Ir(en)_2Br_2]^+$ and *trans*-$[Ir(en)_2I_2]^+$ with excess Cl^- undergo photosubstitution reactions to yield the mixed *trans*-chlorobromo and -chloroiodo complexes, respectively. The yields in these cases are not quantitative, however, because of the formation of the corresponding aquo complexes as well.

Mixed complexes of this type are difficult to prepare by other methods because of the differing *trans*-labilizing effects for the halides (Cl < Br < I).[3] Thus the reaction of *trans*-$[M(en)_2Cl_2]^+$ with bromide or iodide yields the disubstituted complex exclusively. The complexes *trans*-$[Rh(en)_2IX]^+$ (X = Cl, Br) were prepared[3d] with difficulty by the thermal reaction of the diiodo complex with a large excess of X^-. The complexes are also very inert and, especially where M = Ir(III), require extended periods of time at high temperature to effect substitution.[4]

trans-$[Ir(en)_2(H_2O)Cl](ClO_4)_2$ was isolated in 34% yield from an irradiated (Vicor-filtered GEUA11 1200-W lamp) aqueous solution of *trans*-$[Ir(en)_2Cl_2]ClO_4$. The aquo complex was prepared *in situ* photochemically for the preparation of other mixed chlorohalogeno complexes. The compounds prepared and their analyses appear in Table I. The general method of synthesis of *trans*-$[M(en)_2XY]^+$ is given by the reaction scheme


$$\textit{trans}\text{-}[M(en)_2X_2]^+ \xrightarrow[H_2O]{h\nu} \textit{trans}\text{-}[M(en)_2(H_2O)X]^{2+} + X^- \xrightarrow{Ag^+} \underline{AgX} + \textit{trans}\text{-}[M(en)_2(H_2O)X]^{2+}$$
$$\textit{trans}\text{-}[M(en)_2XY]^+ \xleftarrow{Y^-} \textit{trans}\text{-}[M(en)_2(H_2O)X]^{2+} \quad (1)$$

trans-$[Ir(en)_2BrCl]ClO_4$ was isolated in 60% yield by treating a solution of irradiated *trans*-$[Ir(en)_2Cl_2]ClO_4$ with 1 equiv of silver ion to remove the ionic chloride, and then by heating (100°, 30 min) with 1 equiv of bromide ion. *trans*-$[Ir(en)_2ICl]ClO_4$ was similarly prepared in 70% yield by the use of 1 equiv of iodide ion. *trans*-$[Ir(en)_2IBr]ClO_4 \cdot H_2O$ was isolated in 75% yield from an irradiated solution of *trans*-$[Ir(en)_2I_2]ClO_4$ in a procedure similar to those above.

[1] A. W. Adamson, *J. Phys. Chem.*, 71, 798 (1967), and references therein.

[2] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 664 ff.

[3] (a) H. L. Bott, E. J. Bounsall, and A. J. Poë, *J. Chem. Soc.*, 1275 (1966); (b) H. L. Bott and A. J. Poë, *ibid.*, 205 (1967); (c) *ibid.*, 5931 (1965); (d) E. J. Bounsall and A. J. Poë, *ibid.*, 286 (1966).

[4] R. A. Bauer and F. Basolo, unpublished work.