

groups, the former being a net  $\pi$  donor ( $-R$ ) and the latter a net  $\pi$  acceptor ( $+R$ ) substituent.

The precision of the correlation of  $\Sigma\Delta q_{(\pi)}$  vs.  $\sigma_R^0$  is suggestive of a similar correlation<sup>9</sup> of  $\Delta q_{(\pi)}^p$  vs.  $\sigma_R^0$ . The CNDO/2 calculations give somewhat less satisfactory results in that a plot of the excess  $\pi$  charge density at the *para* carbon atom,  $\Delta q_{(\pi)}^p$ , vs.  $\sigma_R^0$  is less precise (RMS = 301; SD = 80; cf. Figure 1). However, the relationship  $\Delta q_{(\pi)}^p \approx 0.7 (\Sigma\Delta q_{(\pi)})$ , is generally a useful approximation of the calculated results. Further, the slope of  $\Delta q_{(\pi)}^p$  vs.  $\sigma_R^0$  (Figure 1) of 0.10e/ $\sigma_R^0$  is of the same order of magnitude as estimated from interpretations of nmr shifts.<sup>9</sup> Since the calculated absolute values of  $\Delta q_{(\pi)}^p$  are actually greater than  $\Sigma\Delta q_{(\pi)}$  for the substituents  $\text{CH}_3$ ,  $\text{CF}_3$ , and  $\text{NO}_2$  (Table I) some small deficiencies of the theory are suggested. Additional features of these calculations as well as those for *meta*- and *para*-substituted fluorobenzenes will be discussed in a subsequent full paper.

**Acknowledgment.** We are pleased to acknowledge the assistance of Dr. Stanton Ehrenson in the indicated modification of Program 91.

(9) (a) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 3146 (1963); (b) G. E. Macie and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2427 (1965); (c) P. C. Lauterbur, *Tetrahedron Lett.*, **8**, 274 (1961); (d) H. Spiesscke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); (e) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960).

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### The Base Hydrolysis of *trans*-[Co(NH<sub>3</sub>)<sub>4</sub><sup>15</sup>NH<sub>3</sub>Cl](ClO<sub>4</sub>)<sub>2</sub> in the Presence of Azide Ion

Sir:

We wish to correct an error reported in a previous communication<sup>1</sup> on the base hydrolysis of *trans*-[Co(NH<sub>3</sub>)<sub>4</sub><sup>15</sup>NH<sub>3</sub>X]<sup>2+</sup> ions (where X = Cl, Br, NO<sub>3</sub>). In one experiment where *trans*-[Co(NH<sub>3</sub>)<sub>4</sub><sup>15</sup>NH<sub>3</sub>Cl](ClO<sub>4</sub>)<sub>2</sub> was treated with NaOH ( $\sim 0.1 M$ ) in the presence of N<sub>3</sub><sup>-</sup> ion ( $\sim 4 M$ ) it was reported that the hydroxo product showed approximately 40% rearrangement to the *cis* form while the [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]<sup>2+</sup> product was 100% *trans*.

The validity of this result has recently been questioned,<sup>2</sup> and we find by repeating the experiment more carefully as previously described that 60% of the product chloride was unreacted chloro complex and that the pmr spectrum originally given was due substantially to the chloro perchlorate. The hydrolysis has now been repeated more carefully with a slightly larger sample of the enriched complex over a longer period. The 100-Mc pmr spectra of the reactant, *trans*-[Co(NH<sub>3</sub>)<sub>4</sub><sup>15</sup>NH<sub>3</sub>Cl](ClO<sub>4</sub>)<sub>2</sub>, and the isolated aquo complex in DMSO are given in Figure 1 (a and b). The spectrum of the aquo complex is essentially unchanged from that found previously<sup>1</sup> and indicates  $\sim 40\%$  rearrangement from *trans* to *cis*. However, the pmr

(1) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 5129 (1967).

(2) We are grateful to Professor F. Nordmeyer for activating our suspicions over this aspect of the original publication.

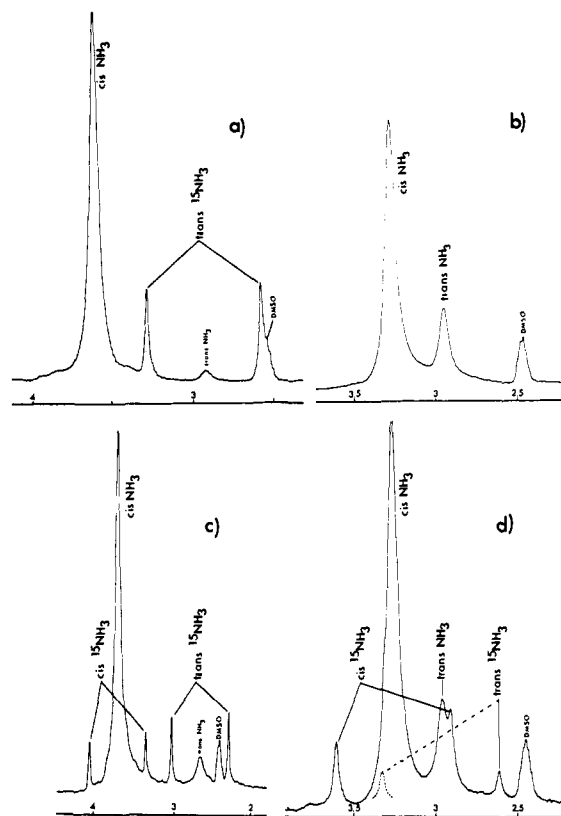


Figure 1. Pmr spectra (100 Mc, scale ppm) for (a) *trans*-[Co(NH<sub>3</sub>)<sub>4</sub><sup>15</sup>NH<sub>3</sub>Cl](ClO<sub>4</sub>)<sub>2</sub>, (b) [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>, (c) *cis*- and *trans*-[Co(NH<sub>3</sub>)<sub>4</sub><sup>15</sup>NH<sub>3</sub>OH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> reaction product, (d) *cis*- and *trans*-[Co(NH<sub>3</sub>)<sub>4</sub><sup>15</sup>NH<sub>3</sub>N<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> reaction product in dimethyl-*d*<sub>6</sub> sulfoxide containing a trace of D<sub>2</sub>SO<sub>4</sub> (98%).

spectrum of the isolated azido complex ( $\epsilon_{\text{max}}$  270) is substantially different from that recorded previously.

Figure 1 (c and d) shows the 100-Mc pmr spectra of the isolated azido complex compared with that for the unenriched [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> complex in DMSO. The signals can be assigned unequivocally by using the 70-cps coupling constant between the <sup>15</sup>NH<sub>3</sub> proton doublet and the symmetry relationship between these signals and those due to the related broad <sup>14</sup>NH<sub>3</sub> protons. Approximately 70% rearrangement is indicated, and this result is more in keeping with that for the hydroxo product and with the results obtained for base hydrolysis of *cis*- and *trans*-[Co(en)<sub>2</sub>NH<sub>3</sub>X]<sup>2+</sup> ions (X = Cl, Br, NO<sub>3</sub>) in the presence of N<sub>3</sub><sup>-</sup>.<sup>3</sup>

The new result does not alter the conclusions reached in the previous article<sup>1</sup> except that it is no longer required that N<sub>3</sub><sup>-</sup> react with the proposed five-coordinate intermediate in a stereospecific manner. In fact, if a trigonal-bipyramidal intermediate obtains, then the stereochemistry of the competition result can be accommodated by an approximately statistical addition of N<sub>3</sub><sup>-</sup> to the edges of the trigonal plane, provided the <sup>15</sup>N label remains in the trigonal plane.

*trans*-[Co(NH<sub>3</sub>)<sub>4</sub>(<sup>15</sup>NH<sub>3</sub>)Cl](ClO<sub>4</sub>)<sub>2</sub> was prepared as described earlier.<sup>1</sup> The complex (1.1 g) was dissolved in 15 ml of dilute HClO<sub>4</sub> (10<sup>-3</sup> M) and added to a solution of NaOH (50 ml, 0.2 N) saturated with NaN<sub>3</sub> at 25°. After 30 min the solution was cooled in an ice bath and excess LiCl was added to precipitate the formed

(3) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, in press.

azido complex (yield 0.12 g). The azido chloride was converted to the perchlorate by treating it with an equivalent amount of  $\text{AgClO}_4$  in water. The  $\text{AgCl}$  was removed and the complex precipitated by adding excess solid  $\text{NaClO}_4$ . The molar absorptivity of the isolated salt,  $[\text{Co}(\text{NH}_3)_4(^{15}\text{NH}_3)\text{N}_3](\text{ClO}_4)_2$ , was  $\epsilon_{518}$  270. The filtrate (ice cold) was treated with cold concentrated  $\text{HBr}$ , and the aquo bromide salt which crystallized was collected, dissolved in water, and adsorbed on an ion-exchange column. Traces of the azido complex were removed by eluting with 1 *M*  $\text{NaClO}_4$ , and the aquo complex was then taken off the column with 3 *M*  $\text{HClO}_4$ . The solution was taken down to a small volume on a vacuum evaporator and the precipitated  $[\text{Co}(\text{NH}_3)_4(^{15}\text{NH}_3)\text{H}_2\text{O}](\text{ClO}_4)_3$  was collected.

The pmr spectra of the complexes were obtained using a Varian HA-100 spectrometer. The samples ( $\sim 0.2$  g/ml) were dissolved in dimethyl- $d_6$  sulfoxide acidified with a trace of  $\text{D}_2\text{SO}_4$  (98 %).

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### Epimerization about Unactivated Tertiary Carbon Atoms in Substituted Cyclopentane Derivatives

Sir:

This report discloses a novel radical epimerization at a tertiary carbon atom in cyclopentane derivatives.

We have observed a slow decrease of the Cotton effect amplitude in the ORD spectrum of a cyclohexane solution of (+)-3-methylcyclopentanone when irradiated with 253.7-m $\mu$  light in the presence of mercuric bromide.<sup>1</sup> After irradiation for 48 hr the amplitude had decreased to 10% of its initial value. The ketone was isolated as its dinitrophenylhydrazone whose  $[\alpha]_D$  value indicated 90% racemization.

On the other hand, almost no racemization was detected when optically active 3-methylcyclohexanone was treated under identical conditions.

Preferential epimerization of a tertiary hydrogen atom bound to a cyclopentane ring was observed on analogous treatment of the steroidal hydrocarbon, 5 $\alpha$ -androstane (**1a**).<sup>2</sup> The only product, the 14 $\beta$ ,5 $\alpha$ -androstane (**2a**), was isolated in ca. 80% yield.<sup>3</sup>

Similar epimerizations at C-14 took place in 5 $\alpha$ -androstane derivatives substituted by acetoxy or carbomethoxy functions in either five- or six-membered rings; e.g., 17 $\beta$ -acetoxy-, 3 $\beta$ ,17 $\beta$ -diacetoxy-, 3 $\alpha$ ,17 $\beta$ -diacetoxy-, and 3 $\beta$ -acetoxy-17 $\beta$ -carbomethoxy-5 $\alpha$ -androstanes **1b-e** gave after irradiation in cyclohexane in the presence of mercuric bromide the corresponding 14 $\beta$  derivatives **2b-e**<sup>4-6</sup> in ca. 80-90% yield.

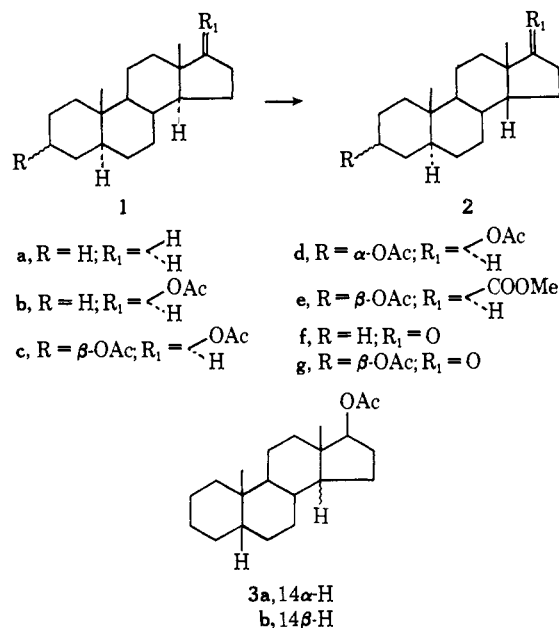
(1) A solution of the ketone (100 ml, 30 mM) in cyclohexane containing 20 mM mercuric bromide was used.

(2) Generally 100 ml of a solution 3 mM in steroid and 3 mM in mercuric bromide was irradiated. Smaller quantities of mercuric bromide were also employed; the minimal concentration which led to the same yield of **2a** was 0.1 equiv with respect to the steroid.

(3) Satisfactory analyses and ir, nmr, and mass spectra were obtained for all new compounds reported.

(4) The characteristic feature in the nmr spectrum of the 17 $\beta$ -acetoxy derivatives in the 14 $\beta$  series is the doublet at 4.8 ppm ( $J = 5$  cps) of the 17 $\alpha$  proton; the corresponding proton in the 14 $\alpha$  series appears as an ill-defined triplet at 4.6 ppm.

(5) The identity of **2c** and **2g** with the authentic samples was proven;



Under the same conditions, both 5 $\alpha$ -17-ketones **1e** and **1f** resulted in the 14 $\beta$ -17-ketones **2f** and **2g**<sup>5,6</sup> (ca. 90%). Furthermore, similar irradiation of 17 $\beta$ -acetoxy-5 $\beta$ -androstane (**3a**), possessing hydrogen atoms in both *trans*-hydrindan and *cis*-decalin ring junctions, yielded the 5 $\beta$ ,14 $\beta$  derivative **3b**, indicating a preferential epimerization at the former junction.

The reversibility of the C-14 epimerizations was proved by irradiation of the 14 $\beta$  steroid **2a**, which gave ca. 5% of the 14 $\alpha$  derivative **1a**. The >9:1 ratio may thus reflect the relative stability of the two C-14 epimers in androstane and 17-substituted androstane systems.<sup>7</sup> We assume that these epimerizations are radical induced, the radicals being formed on irradiation of mercuric bromide in cyclohexane solution.

Mercuric bromide, which is soluble in cyclohexane to the extent of  $\sim 120$  mg/l. at ambient temperature, has absorption maxima at 198 and 236 m $\mu$  ( $\epsilon$  15,000 and 2400).<sup>8</sup> On irradiation with 253.7-m $\mu$  light it slowly decomposes to mercurous bromide and subsequently to mercury metal.

Neither irradiation in the presence of mercurous bromide nor irradiation in the presence of mercury metal (or cyclohexylmercuric bromide) affected the C-14 position of a 14 $\alpha$  steroid. Similarly, irradiation of the 14 $\alpha$  compounds with light of longer wavelength in the presence of mercuric bromide is ineffective.

Thus it appears that the direct excitation of the latter compound released bromine radicals which are capable of preferential extraction of tertiary hydrogen atoms of substituted cyclopentanes.

A complete suppression of the epimerizations in the presence of oxygen, cyclohexane, or phenol<sup>9</sup> indicated

cf. A. F. St. Andre, H. B. McPhiliamy, J. A. Nelson, A. C. Shabica, and C. R. Scholtz, *J. Amer. Chem. Soc.*, **74**, 5506 (1952).

(6) Irradiation of **1f** and **1g** gave in addition small amounts of 17-oxo-13 $\alpha$ -5 $\alpha$ -androstanes and 17-oxo-13 $\alpha$ -3 $\beta$ -acetoxy-5 $\alpha$ -androstane, respectively.

(7) For a discussion of the relative stability relationship of the C/D *trans* and *cis* rings in steroids, cf. M. Hanack, "Conformation Theory," Academic Press, New York, N. Y., 1965, pp 216-225, and references cited therein.

(8) The reported uv values for mercuric bromide in ethanol solution are  $\lambda_{\text{max}}$  206, 234 m $\mu$  ( $\log \epsilon$  3.64, 3.79): B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 1454 (1955).