

closest-packed. The two exceptions are europium and ytterbium, which form orthorhombic dihydrides.<sup>2</sup> We wish to report the synthesis of a noteworthy higher hydride of ytterbium.

For our investigations of rare-earth hydrogen systems in regions of high dissociation pressures (up to 65 atm.), we constructed a stainless steel high-pressure system. This consisted of an atomic hydrogen welded,<sup>3</sup> double-walled bomb, in which the outer chamber could be pressured with hydrogen to prevent diffusion from the inner bomb at the high temperatures. Accessories consisted of a 0–1000 p.s.i. Bourdon gauge and a steel reservoir of uranium hydride for pressuring the system.

The ytterbium–hydrogen system was of particular interest since it seemed likely that the predicted thermodynamic stability of a trihydride phase placed it within range of attainable high pressures. The inner bomb was charged with eight grams of cleaned, 99.8% ytterbium metal<sup>4</sup> and first heated *in vacuo*. It then was allowed to absorb hydrogen at atmospheric pressure until the composition of the hydride was YbH<sub>1.90</sub>. The hydrogen pressure in the apparatus was increased to several atmospheres and pressure–temperature–composition data obtained. At a composition of YbH<sub>2.4</sub> the dissociation pressure was 20.9 atm. at 312°. Upon completion of the experiments, the sample was removed from the bomb in a protective atmosphere. It was a black, air-stable substance; a 94 mg. sample stored in air for 70 days gained less than 1 mg. Examination by powder X-ray diffraction techniques showed the presence of a f.c.c. phase along with a small amount of the orthorhombic dihydride. The lattice constant of the f.c.c. phase was determined, after correction for film shrinkage, from a plot of *a* versus the Nelson–Riley function, and found to be  $5.192 \pm 0.002$  Å. A calculation of the expected lattice constant for a f.c.c., BiF<sub>3</sub>-type ytterbium trihydride using 0.86 Å. for the radius of the Yb<sup>+3</sup> ion<sup>5</sup> and correcting for the increased coordination number, and 1.29 Å. for the radius of the hydride ion<sup>6</sup> gave *a* = 5.14 Å.

Additional portions of the sample were analyzed for hydrogen by three methods: one portion by combustion of the hydride in a stream of oxygen, one portion by thermal decomposition and measurement of the hydrogen evolved, and several portions by reaction of the hydride with acid to give an amount of hydrogen which could be accurately measured. The formula was found to be YbH<sub>2.55 ± 0.06</sub>. The f.c.c. phase then would correspond ideally to the compound YbH<sub>3</sub>, and thus unexpectedly be analogous to the trihydrides of the lighter rare-earths.

It was verified by an X-ray diffraction powder photograph that thermal decomposition of YbH<sub>2.55</sub> in hydrogen at approximately one atmosphere yielded the orthorhombic dihydride. The formula of the dihydride was found to be YbH<sub>1.95 ± 0.05</sub>, by measurement of the hydrogen evolved from the

(2) W. L. Korst and J. C. Warf, *Acta Cryst.*, **9**, 452 (1956).

(3) T. R. P. Gibb, Jr., J. J. McSharry and R. W. Bragdon, *J. Am. Chem. Soc.*, **73**, 1751 (1951).

(4) Purchased from Research Chemicals, Burbank, California.

(5) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954).

(6) G. Libowitz and T. R. P. Gibb, Jr., *ibid.*, **60**, 510 (1956).

YbH<sub>2.55</sub>, as well as by analysis of the resulting dihydride. A metastable f.c.c. modification of ytterbium dihydride with *a* 5.26 Å. also was found when samples of YbH<sub>2.55</sub> were thermally decomposed and quenched.

Measurement of the magnetic susceptibility of the YbH<sub>2.55</sub> at room temperature by the Gouy method gave a molar susceptibility of  $5040 \times 10^{-6}$  c.g.s. unit. This compares quite reasonably with the value  $7260 \times 10^{-6}$  c.g.s. unit/mole<sup>7</sup> which would be expected for a hypothetical YbH<sub>3</sub>, containing only Yb<sup>+3</sup> and H<sup>-</sup> ions.

We also attempted to prepare a higher europium hydride by treating two small (30 mg.) pieces of the metal with hydrogen in the high-pressure apparatus in two separate experiments (33–41 atm. and 400–500°), but both attempts resulted only in the formation of the orthorhombic EuH<sub>1.8–1.9</sub>. Perhaps EuH<sub>3</sub> was formed, but reverted to the dihydride when ordinary conditions were restored. It is also possible, since europium(II) is thermodynamically more stable than ytterbium(II) relative to the respective trivalent states, that no EuH<sub>3</sub> phase could be formed under the prevailing conditions. We succeeded, however, in preparing another sample of the higher ytterbium hydride from approximately 100 mg. of ytterbium metal. An X-ray diffraction powder photograph of the resulting hydride showed the presence of a large portion of the orthorhombic YbH<sub>2</sub> along with the f.c.c. phase. Analysis of a portion of this product gave the formula YbH<sub>2.2</sub>.

We are pleased to acknowledge the financial support of the Office of Naval Research.

(7) G. Hughes and D. W. Pearce, *ibid.*, **55**, 3277 (1933).

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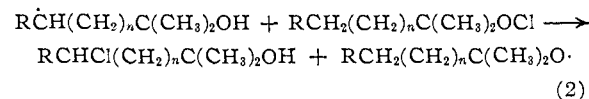
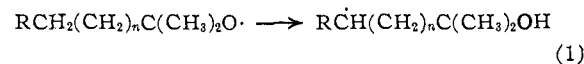
KENNETH HARDCASTLE

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#### INTRAMOLECULAR CHLORINATION WITH LONG CHAIN HYPOCHLORITES<sup>1</sup>

Sir:

As part of our study of the radical reactions of alkyl hypochlorites<sup>2,3</sup> we have been investigating the possibility of rearrangement of long-chain alkyl hypochlorites to chloroalcohols analogous to Hofmann–Löffler–Freitag reaction of N-chloroamines<sup>4</sup> *via* a radical chain process involving sequences such as



(1) Work supported in part by a Grant from the National Science Foundation.

(2) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960).

(3) C. Walling and W. Thaler, *ibid.*, in press.

(4) Conclusive proof of the radical chain nature of the Hofmann–Löffler–Freitag reaction and a review of older work has been given by E. J. Corey and W. R. Hertler, *ibid.*, **82**, 1657 (1960).

The existence of such a process in competition with intermolecular reactions or cleavage of the intermediate alkoxy radical would be of interest, since Corey<sup>4</sup> has suggested that the intramolecular nature of the N-chloramine reaction may arise from a positive charge on the intermediate radical which is here lacking.<sup>5</sup> Also, since preferential attack through a quasi-six membered transition state ( $n = 2$  in reaction 1) would be anticipated,<sup>5</sup> the reaction should provide a convenient synthesis of  $\delta$ -chloroalcohols and accordingly a variety of substituted tetrahydrofurans.

We find that a number of long chain *t*-hypochlorites indeed undergo photodecomposition in  $\text{CCl}_4$  or  $\text{C}_2\text{Cl}_4\text{F}_2$  to give the expected  $\delta$ -chloroalcohols as indicated in Table I. The reaction evidently involves long chains, since the solutions are stable in the dark, but the color of the hypochlorite disappears rapidly at  $0^\circ$  on illumination with an incandescent lamp. Products were separated by gas-liquid chromatography and the chloroalcohols identified by infrared spectra and conversion to the corresponding tetrahydrofurans by alcoholic potassium hydroxide, then analysis or comparison with known samples.

TABLE I  
PHOTODECOMPOSITION OF HYPOCHLORITES  $\text{RC}(\text{CH}_3)_2\text{OCl}$   
(AT  $0^\circ$  IN  $\text{CCl}_4$ , UNLESS INDICATED)

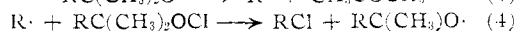
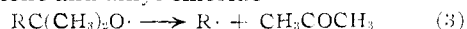
R-	Concn. (molar)	Products (% yield) <sup>a</sup>
1 $\text{CH}_3-$	2.6	$\text{CH}_3\text{Cl}$ , acetone (97)
2 $\text{C}_2\text{H}_5-$	1.5	$\text{C}_2\text{H}_5\text{Cl}$ , acetone (96)
3 $n\text{-C}_3\text{H}_7-$	1.8	$\text{C}_3\text{H}_7\text{Cl}$ , acetone (59)
		$\text{Cl}(\text{CH}_2)_3\text{C}(\text{CH}_3)_2\text{OH}$ (17)
	1.8 ( $40^\circ$ )	$\text{C}_3\text{H}_7\text{Cl}$ , acetone (63)
		$\text{Cl}(\text{CH}_2)_3\text{C}(\text{CH}_3)_2\text{OH}$ (16)
	1.8 ( $80^\circ$ )	$\text{C}_3\text{H}_7\text{Cl}$ , acetone (68)
		$\text{Cl}(\text{CH}_2)_3\text{C}(\text{CH}_3)_2\text{OH}$ (15)
4 $(\text{CH}_3)_2\text{CHCH}_2-$	1.6	<i>i</i> - $\text{C}_4\text{H}_9\text{Cl}$ , acetone (43)
		$\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ (29)
	1.6 ( $40^\circ$ )	<i>i</i> - $\text{C}_4\text{H}_9\text{Cl}$ , acetone (48)
		$\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ (27)
	1.6 ( $80^\circ$ )	<i>i</i> - $\text{C}_4\text{H}_9\text{Cl}$ , acetone (55)
		$\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ (26)
5 $n\text{-C}_4\text{H}_9-$	1.7	<i>n</i> - $\text{C}_4\text{H}_9\text{Cl}$ , acetone (13)
		$\text{CH}_3\text{CHClCH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ (80)
	0.8 ( $\text{C}_2\text{Cl}_4\text{F}_2$ )	<i>n</i> - $\text{C}_4\text{H}_9\text{Cl}$ , acetone (15)
		$\text{CH}_3\text{CHClCH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ (76)
	3.2 ( $\text{C}_2\text{Cl}_4\text{F}_2$ )	<i>n</i> - $\text{C}_4\text{H}_9\text{Cl}$ , acetone (13)
		$\text{CH}_3\text{CHClCH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ (77)
	6.7 ( $\text{C}_2\text{Cl}_4\text{F}_2$ )	<i>n</i> - $\text{C}_4\text{H}_9\text{Cl}$ , acetone (14)
		$\text{CH}_3\text{CHClCH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ (73)

<sup>a</sup> Major products only, yields  $\pm 5\%$  of indicated values.

The intramolecular nature of the hydrogen abstraction step in the rearrangement was demonstrated for compound 5 by examining the competition with the unimolecular decomposition of the intermediate alkoxy radical as a function of concentration. No significant variation of yields with concentration was found and it is notable that the intramolecular reaction remains the major path even in 6.7 *M* solution.

(5) The possibility of such a reaction in the steroid series has been suggested by D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, *J. Am. Chem. Soc.*, **82**, 2640 (1960), and, we understand, recently observed, D. H. R. Barton, *ibid.*, **83**, 2213 (1961).

Cleavage of the intermediate alkoxy radical to yield acetone and alkyl chloride



is the most serious side-reaction,<sup>6</sup> and varies with hypochlorite structure in a predictable manner. With  $\text{R} < \text{C}_3$  it is essentially the sole reaction in keeping with our failure to detect any  $\beta$  or  $\gamma$ -chloroalcohols from longer chain hypochlorites. In hypochlorites containing  $\delta$ -hydrogen, more cleavage occurs when intramolecular attack must be on primary hydrogen than when it is on a secondary hydrogen. Assuming the rates of cleavage of alkoxy radicals from 3, 4 and 5 are the same we may calculate relative reactivities per H for the abstraction process as 0.028, 0.036 and 1.0, respectively, at  $0^\circ$ , a greater difference than would be predicted from the relative reactivities of primary and secondary hydrogens in intermolecular *tert*-butyl hypochlorite chlorinations (1:17 at  $0^\circ$ ).<sup>7</sup>

Since the amount of cleavage increases with temperature, our yields of chloroalcohols presumably could be improved at lower temperatures. For hypochlorite<sup>4</sup> the variation in product ratio with temperature indicates  $E_{\text{cleavage}} - E_{\text{abstraction}} = 0.8$  kcal., together with a slightly larger *PZ* factor for the cleavage. Actually the difference in *PZ* factors is surprisingly small considering that intramolecular hydrogen abstraction requires a sharply defined cyclic transition-state.

We have detected no  $\epsilon$ -chloroalcohol from hypochlorite.<sup>5</sup> Here its formation would require attack on a primary H, and we are currently examining more favorable cases.

We also have examined the products from the photodecomposition of the primary and secondary hypochlorites from 1-pentanol and 2-hexanol. Valeraldehyde and 2-hexanone are major products, and chlorine appears to be liberated during the reaction (presumably from HCl and ROCl) so that the process loses its intramolecular character. Higher boiling products are formed as well, and their structure is being studied, as well as the possibility of favoring the intramolecular reaction by changes of reaction conditions.

(6) Reaction (3) is considerably more rapid when  $\text{R} =$  a higher alkyl group than when  $\text{R} = \text{CH}_3$ , cf. P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).

(7) Our earlier value at  $40^\circ$  has been redetermined as 12.1:1<sup>12</sup> proportional adjustment of the old value at  $0^\circ$  gives 17:1.

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#### POTENTIAL ANTICANCER AGENTS. I. LXI. A NOVEL SYNTHESIS OF "SPONGO" NUCLEOSIDES

Sir:

Interest in nucleosides derived from  $\beta$ -D-arabinofuranose that can undergo anabolism by enzymes

(1) This work was carried out under the auspices of the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institutes of Health, Public Health Service, Contract No. SA-43-ph-1892. The opinions expressed in this paper are those of the authors and are not necessarily those of the Cancer Chemotherapy National Service Center. For the preceding paper in this series, see L. O. Ross, E. M. Acton, W. A. Skinner, L. Goodman and B. R. Baker, *J. Am. Chem. Soc.*, **83**, in press (1961).