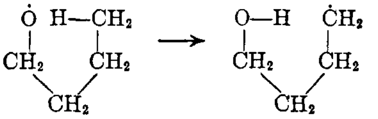
in the decomposition of primary and secondary hypochlorites.[3]

We have found that *n*-butyl hypochlorite upon thermal or photochemical decomposition gives tetramethylene chlorohydrin. We believe that this product is formed by the intramolecular abstraction of a δ-hydrogen atom in an alkoxy free radical.

$$n\text{-}C_4H_9OCl \xrightarrow[\text{or } \Delta]{h\nu} n\text{-}C_4H_9O\cdot + Cl\cdot \qquad (1)$$

(initiation)



(intramolecular hydrogen abstraction) (2)

$$HO(CH_2)_4\cdot + n\text{-}C_4H_9OCl \longrightarrow HO(CH_2)_4Cl + n\text{-}C_4H_9O\cdot \qquad (3)$$

(chain propagation)

Classical studies[6,7] on the decomposition of primary and secondary hypochlorites indicated that carbonyl compounds, aldehydes and ketones, respectively, were the principal products. For this reason we expected that butyraldehyde might be an important side product in the present studies. Only traces of the aldehyde were found but a considerable quantity of butyl butyrate was obtained. The ester may have been produced from butyraldehyde or alternatively from intermediates which under other conditions would lead to aldehyde.

An interesting observation made in the course of this work was that butyl hypochlorite easily effected the chlorination of the unactivated benzene nucleus. Chlorobenzene was obtained in high yield at room temperature with acetic acid as solvent and sulfuric acid as catalyst.

EXPERIMENTAL

n-Butyl hypochlorite was prepared by adding 67 ml. of *n*-butyl alcohol, 400 ml. of benzene, and 67 ml. of acetic acid to a mixture of 1000 ml. of 0.76*M* sodium hypochlorite and 200 g. of ice. The benzene solution of *n*-butyl hypochlorite was separated, and the aqueous fraction was washed twice with 50-ml. portions of benzene. The combined benzene solution was washed with aqueous sodium bicarbonate and dried over anhydrous sodium sulfate. The resulting dry benzene solution (550 ml.) was 1.14*M* in *n*-butyl hypochlorite, as determined by iodometric titration. Seventy grams of dry powdered sodium bicarbonate was added, and the resulting slurry was heated under reflux with agitation until the evolution of carbon dioxide ceased (1 hr.). The solids were removed by filtration and the benzene was distilled. Butanol was detected by gas chromatography in the distillate. The residue was fractionally distilled and the fractions were assayed by gas chromatography.

			Composition	
Weight, G.	B.P./Mm.	n_D^{25}	Tetramethylene chlorohydrin, %	Butyl butyrate, %
1. 4.7	35–50°/12	1.4119	4	45
2. 8.6	54–71°/8	1.4278	32	40
3. 9.2	38–50°/~1	1.4465	83	—
4. 7.0	Pot residue	1.4712		

The calculated yield of tetramethylene chlorohydrin was 16%. The infrared spectrum of Fraction 3 confirmed that it was chiefly tetramethylene chlorohydrin. When a portion of Fraction 3 was treated with hot aqueous 10*M* sodium hydroxide, tetrahydrofuran, b.p. 60–68°, n_D^{25} 1.4030, was obtained. The crude tetrahydrofuran was dried and identified by its infrared spectrum.

Butyl butyrate was obtained in approximately 20% yield. Butyraldehyde, the product expected from earlier studies in hypochlorite decomposition, was substantially absent.

In a similar experiment, conducted in the absence of sodium bicarbonate, the total reaction mixture was treated with potassium hydroxide and tetrahydrofuran was obtained directly. In another experiment, a 4*M* solution of *n*-butyl hypochlorite in carbon tetrachloride was exposed to a high-intensity ultraviolet light (General Electric AH-6 high-pressure 1000-watt mercury arc) for 7 sec., whereupon the hypochlorite decomposed completely. The exothermic reaction raised the temperature from 25° to the boiling point of the mixture (~80°). The resulting mixture contained 10% tetramethylene chlorohydrin. The synthesis of tetramethylene chlorohydrin was also carried out in the vapor phase. A stream of nitrogen saturated with *n*-butyl hypochlorite at 0° was exposed to an AH-6 lamp and the products condensed in a trap cooled by solid carbon dioxide. Here again tetramethylene chlorohydrin was demonstrated by gas chromatography.

Incidental to these studies, it was observed that *n*-butyl hypochlorite, like *t*-butyl hypochlorite,[8] brought about the facile acid-catalyzed chlorination of an unactivated aromatic nucleus. When sulfuric acid (3 ml.) was added to 335 ml. of a 1*M* solution of *n*-butyl hypochlorite in benzene–acetic acid (1:2) an exothermic reaction occurred. Distillation of the benzene solution, after the acetic acid had been removed by cold aqueous alkali, gave chlorobenzene and butyl acetate in substantially quantitative yields.

Contribution No. 713
Central Research Department
Experimental Station
E. I. du Pont de Nemours and Co.
Wilmington, Del.

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Acid-Catalyzed Rearrangements of Nopinic Acid

Werner Herz and H. J. Wahlborg[1]

Received October 5, 1961

Treatment of nopinic acid (I) with mineral acid gives rise to two products, depending on the acid used.[2] Fission with hydrogen bromide in acetic

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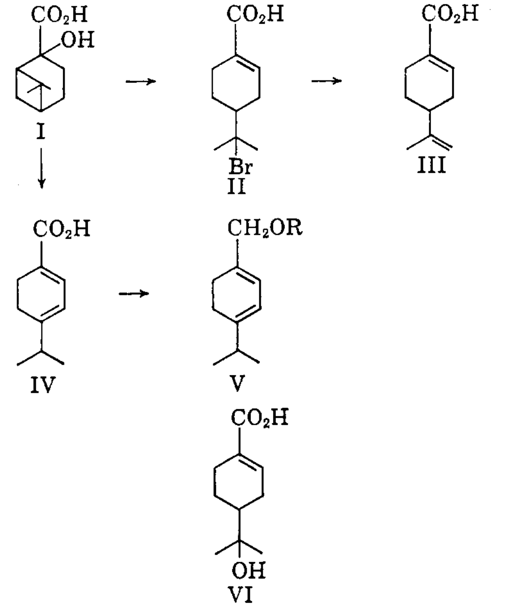
(1) Supported in part by a grant from the National Science Foundation (G-14396).

(2) For a review of early work, see J. L. Simonsen, *The Terpenes*, Cambridge University Press, Vol. 2, p. 193 (1949).

acid leads to formation of a bromotetrahydrocumic acid which can be converted to a dihydrocumic acid with base. Kergomard[3] recently showed that the latter was perillic acid (III) by an analysis of the infrared spectrum and synthesis from perillyl alcohol. Infrared evidence was also adduced in favor of formulating the intermediate bromo acid as II. Furthermore, Kergomard suggested that an isomeric dihydrocumic acid obtained by digesting nopinic acid with dilute sulfuric acid might be IV, again because of the infrared spectrum.



We have studied these compounds further to place the postulated structures on a more secure footing. The ultraviolet spectra (λ_{max} 215.5 mμ, ϵ 12400) of the bromotetrahydrocumic acid and of its dehydrohalogenation product (λ_{max} 216.5 mμ, ϵ 12000) completely support formulas II and III proposed by Kergomard, as do the NMR spectra. II (in trifluoroacetic acid solution) displays one vinyl proton signal centered at 438 c.p.s.[4] and two slightly nonequivalent singlet methyls at 108.3 and 110.6 c.p.s. (deshielding by the α-bromine atom). III has three vinyl protons and one vinyl methyl singlet at 101 c.p.s. When II was dehydrohalogenated with potassium methoxide, purification of the product resulted in the isolation of a small amount of the previously undescribed VI, λ_{max} 216 mμ (ϵ 10200), significant NMR signals (trifluoracetic acid) at 450 c.p.s. (one vinyl proton) and 100 c.p.s. (six protons, two methyl groups deshielded by neighboring hydroxyl).

The acid obtained by sulfuric acid treatment of nopinic acid had an ultraviolet spectrum characteristic of a 2,4-dienoic acid (λ_{max} 298.5 mμ, ϵ 7000). Its NMR spectrum (trifluoroacetic acid) was compatible with formula IV (two vinyl proton doublets at 440 and 446 c.p.s., β-proton, and 356 and 362 c.p.s., α-proton; methyl signals-intensity six protons at 63 and 71 c.p.s.), but it did not react with maleic anhydride, or tetracyanoethylene (deactivation of the diene system by the carboxyl group). Reduction with lithium aluminum hydride gave 1-hydroxymethyl-4-isopropyl-1,3-cyclohexadiene (V. $\mathrm{R} = \underset{\underset{\mathrm{O}}{|}}{=\mathrm{C}}=\mathrm{CH_3}$ λ_{max} 266 mμ, ϵ 5200) which smoothly underwent the Diels-Alder reaction with tetracyanoethylene, thus establishing the proposed structure.

EXPERIMENTAL[5]

Nopinic acid. The oxidation of β-pinene,[6] n^{25}_{D} 1.4760, $[\alpha]^{24}_{D}$ −17.4, was carried out as described by Winstein and Holness,[7] but the yields were variable and consistently lower than reported.

Bromotetrahydrocumic acid (II). This substance was prepared by the method of Kergomard,[3] yield 6.5 g., m.p. 160–164°, from 13.5 g. of nopinic acid. Crystallization from chloroform-hexane raised the m.p. to 171–173°.

Perillic acid (III). A solution of 2.8 g. of II in 20 ml. of methanol containing 2.24 g. of potassium hydroxide was warmed on the steam bath for a few minutes, cooled, diluted with water, filtered, and acidified. The crude product, wt. 1.65 g., was recrystallized repeatedly from ethanol-water and then melted at 129–130°.

When the dehydrohalogenation was carried out with an equivalent amount of potassium methoxide in methanol, the m.p. of the product could not be raised above 115°. The mother liquors were combined, concentrated, cooled, filtered, and extracted with ether. The dried ether extracts yielded a solid, m.p. 145–154°, which was recrystallized from ether-hexane to give VI, m.p. 154–156°.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.20; H, 8.74; O, 26.06. Found: C, 64.94; H, 8.59; O, 25.97.

Dihydrocumic acid (IV). Heating a solution of 35 g. of nopinic acid sodium salt, 1200 ml. of 25% sulfuric acid, and 1200 ml. of water on the steam bath for 4 hr. yielded, after cooling and crystallization from aqueous ethanol, 11 g. of IV, m.p. 123–127°. Further recrystallization raised the m.p. to 133–136°.

Reduction of 10 g. of IV with lithium aluminum hydride in ether solution with lithium aluminum hydride resulted in a neutral fraction b.p. 65–82° (0.5 mm.), wt. 5 g., which was redistilled twice. A center cut, b.p. 80° (0.8 mm.), was analyzed, but analysis and infrared spectrum still indicated the admixture of a small amount of a carbonyl-containing fraction.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.94; H, 10.59. Found: C, 77.75; H, 10.29.

The alcohol V, wt. 5.2 g., was acetylated with acetic anhydride in pyridine in the usual fashion. The neutral fraction was dried and distilled, yield 4 g., b.p. 90° (1.2 mm.).

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(3) A. Kergomard, *Bull. Soc. Chim.*, 1161 (1957).

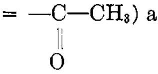
(4) NMR spectra were run by Mr. Fred Boerwinkle in trifluoroacetic acid solution at 60 mc., using tetramethylsilane as internal standard. Frequencies were determined by the side-band technique. The Varian HR-60 instrument used was purchased with funds provided by the Molecular Biophysics Institute of the Florida State University.

(5) M.p.'s and b.p.'s are uncorrected. Analyses by Dr. F. Pascher, Bonn, Germany. Ultraviolet spectra were determined by Mrs. P. DeTar on a Cary Model 14 recording spectrophotometer in 95% ethanol solution.

(6) Kindly furnished by Dr. J. H. Stump, Newport Industries Company, Pensacola, Fla.

(7) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.* 77, 3054 (1955).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.22; H. 9.31.

A mixture of 1.0 g. of V (R =  $-\underset{\underset{O}{\|}}{C}-CH_3$) and 0.66 g. of tetracyanoethylene in 20 ml. of benzene was refluxed for two hours, cooled, diluted with 20 ml. of ligroin, and refrigerated. There separated 1.0 g. of product, m.p. 141–143°, which was recrystallized from benzene–petroleum ether and then melted at 144–145°.

Anal. Calcd. for $C_{16}H_{18}N_4O_2$: C, 67.08; H, 5.61; N, 17.29. Found: C, 67.03; H, 5.73; N, 16.95.

DEPARTMENT OF CHEMISTRY
THE FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLA.

Reactions Catalyzed by Potassium Fluoride. II. The Conversion of Adipic Acid to Cyclopentanone

LEON RAND, WALTER WAGNER, PETER O. WARNER, AND L. ROBERT KOVAC

Received September 29, 1961

A preliminary communication[1] recently reported the apparent function of anhydrous potassium fluoride as a base in the Hofmann reaction converting *N*-chlorobenzamide to phenyl isocyanate. This unexpected behavior of potassium fluoride became the object of further study in an attempt to determine whether the salt behaved similarly in other reactions.

The literature cites a few examples of the use of potassium fluoride which include several catalytic decarboxylation reactions[2] and a series of addition-dehydration reactions of active methylene-containing compounds.[3] Each of the reported reactions is classically base-catalyzed, either to form initially a carboxylate ion or a carbanion, suggesting that hydrogen fluoride is evolved as a by-product. Moreover, each reaction reported employed an essentially equimolar amount of potassium fluoride.

It was decided to study in greater detail the conversion of adipic acid to cyclopentanone because of its relative simplicity. In a series of experiments in which the amount of potassium fluoride was decreased relative to the concentration of adipic acid, it was found that the yield of cyclopentanone increased, although the rate of reaction was slower (Table I).

TABLE I

AFFECT OF POTASSIUM FLUORIDE CONCENTRATION ON YIELD OF CYCLOPENTANONE

Mole Ratio of Adipic Acid/KF	% Yield of Cyclopentanone
1:2	23
1:1	31
2:1	37
4:1	54
20:1	81

The absence of any potassium fluoride in a reaction carried out under the same conditions failed to produce any ketone.

A quantitative examination provided further pertinent data. The determination of the amounts of volatile products, according to Equation 1,

$$HOOC{-}(CH_2)_4{-}COOH \longrightarrow C_5H_8O + CO_2 + H_2O \quad (1)$$

indicated that each product was formed in equimolar quantities, the ratio of ketone: carbon dioxide: water being 1:1.19:1.06. This suggests the absence of any appreciable side reactions, such as the formation of cyclopentene, as had been reported in an earlier study,[4] or any appreciable elimination of hydrogen fluoride. This analytical data also precludes the formation of adipic anhydride as an intermediate in the formation of cyclopentanone since it has been shown that the anhydride decomposes spontaneously to a polymer.[5] The small amount of basic catalyst required had already been illustrated, since not only will the reaction occur with much less than a molar equivalent of barium hydroxide,[6] but it proceeds also in high yield when the adipic acid is distilled from jena glass,[4] which contains basic salts of barium and calcium.

A mechanism for this reaction has been postulated by Neunhoeffer and Paschke[4] which requires the abstraction of an α-hydrogen followed by a Dieckmann condensation. Since potassium fluoride, which is capable of abstracting a proton from an acid and still retain bonding,[7] does not appear to be a strong enough nucleophile to react with the α-hydrogen, it was felt that either the cyclopentanone formation using barium hydroxide followed a different path than when potassium fluoride was employed, or that abstraction of the α-hydrogen was not a necessary step. It was of interest, therefore, to attempt the formation of 2,2,5,5-tetramethylcyclopentanone from 2,2,5,5-tetramethyl-

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