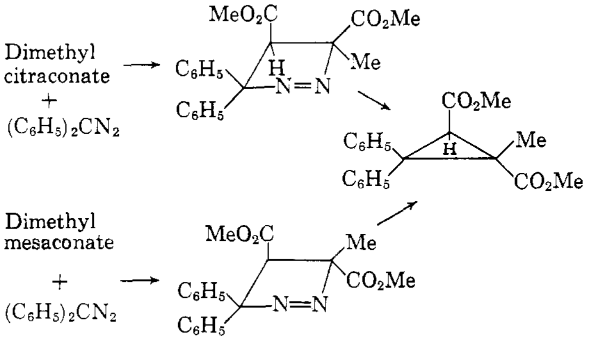
any trace of an N—H absorption in their infrared spectra, there can be little doubt that the double bond is between the two nitrogens in each isomer. Furthermore, although the two carbomethoxy groups in the two isomers have most likely retained the geometrical relationship of their precursor diesters, the fact that they are geometrical isomers is sufficient for the point in which we were primarily interested—the stereochemistry of their decomposition to cyclopropanes.

The two 1-pyrazolines were then decomposed slightly above their melting points and it was found that both gave, within experimental error, the same reaction mixture. Furthermore, the product was, so far as we could detect, exclusively the dimethyl ester of 3,3-diphenyl-1-methylcyclopropane-1,2-dicarboxylic acid in which the two carboalkoxy groups are trans.[3]



Thus, in the case examined by van Alphen, formation of the 5,5-diphenyl-1-pyrazoline is apparently stereospecific, and the loss of stereospecificity in this reaction series actually occurs during the decomposition step.

EXPERIMENTAL[5]

Preparation of 3-methyl-cis-3,4-dicarbomethoxy-5,5-diphenyl-1-pyrazoline. To 10 g. (0.0556 moles) of dimethyl citraconate[6] was added 10.8 g. (0.0556 moles) of crystalline diphenyldiazomethane[7] obtained from the oxidation of benzophenone hydrazone. The resultant solution was allowed to remain at room temperature with occasional shaking for one week. The slightly pink mixture was then filtered and the resulting solid was washed with ether. Three recrystallizations from methyl alcohol gave 8.4 g. (43.0% yield) of colorless solid, m.p. 124° dec., reported m.p. 123° dec. The infrared spectrum showed no absorption in the 3-μ region.

Anal. Calcd. for $C_{20}H_{20}N_2O_4$: C, 68.18; H, 5.68; N, 7.95. Found: C, 67.81; H, 5.95; N, 8.08.

Decomposition of 3-Methyl-cis-3,4-dicarbomethoxy-5,5-diphenyl-1-pyrazoline. A sample (0.237 g., 0.663 mole) of the pyrazoline was heated at 125° (just above its melting point) until nitrogen evolution had ceased. The decomposition product, a white solid, weighed 0.217 g. (equivalent to 0.670 mole of the corresponding cyclopropane). Recrystallization of the product from ethyl alcohol gave colorless needles, m.p. 114–115° (reported m.p. 115°), which did not decolorize potassium permanganate solution. The infrared spectrum of the crude material and the recrystallized material were virtually identical.

Preparation of 3-methyl-trans-3,4-dicarbomethoxy-5,5-diphenyl-1-pyrazoline. To 10 g. (0.0556 mole) of dimethyl mesaconate was added 10.8 g. (0.0556 mole) of diphenyldiazomethane. The resultant solution was mixed thoroughly and allowed to remain at room temperature for 1 week. The resulting greenish solid was washed well with ether and recrystallized from methanol to yield 9.1 g. (46.4%) of white crystals; m.p. 104° dec. The infrared spectrum showed no absorption in the 3-μ region.

Anal. Calcd. for $C_{20}H_{20}N_2O_4$: C, 68.18; H, 5.68; N, 7.95. Found: C, 68.28; H, 5.71; N, 8.22.

Decomposition of 3-methyl-trans-3,4-decarbomethoxy-5,5-diphenyl-1-pyrazoline. A sample of 0.192 g. (0.546 mmole) of of the 1-pyrazoline was heated above its melting point until nitrogen evolution had ceased. The decomposition product, a white solid, weighed 0.177 g. (corresponding to 0.545 mmole of the cyclopropane). Recrystallization of the product from methyl alcohol yielded colorless, crystalline needles, m.p. 115°. Admixture with the decomposition product from 3-methyl-cis-3,4-dicarbomethoxy-5,5-diphenyl-1-pyrazoline showed no depression in melting point. Furthermore, the infrared spectra of the two crude reaction products were identical and the infrared spectrum of the crude reaction product and the recrystallized product were identical.

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[5] Melting points are uncorrected.

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Intramolecular Hydrogen Abstraction in a Primary Alkoxy Radical

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It has been established that the Hoffman-Löffler-Freytag reaction, in which an *N*-haloamine is converted to the corresponding pyrrolidine, is a free-radical chain process depending on the intramolecular abstraction of a δ-hydrogen atom by a nitrogen free radical.[1] Recently a similar intramolecular hydrogen abstraction has been observed in the decomposition of long-chain tertiary hypochlorites.[2–5] It was reported that no analogous intramolecular reaction was observed

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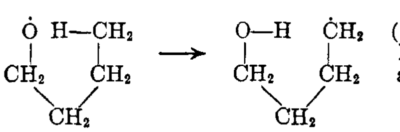
in the decomposition of primary and secondary hypochlorites.[3]

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.

Weight, G.	B.P./Mm.	n_D^{25}	Composition 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.

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Acid-Catalyzed Rearrangements of Nopinic Acid

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