dinitrophenylhydrazone, isobutyraldehyde 2,4-dinitrophenylhydrazone and isovaleraldehyde 2,4-dinitrophenylhydrazone, identified by the m. p. and the m. p. of mixtures with authentic samples, were thus obtained from the three amino acids, respectively; yield about 20%. A solid formed in the reaction flask proved to be uramil. When a mixture of alanine (0.2 g.) and alloxantine (0.5 g.) in water (50 cc.) was heated, carbon dioxide was detected, as well as ammonia if excess of sodium hydroxide was added.

Reaction of Alloxantine with Amines.—Alloxantine (1 g.), ethylamine (3 g.), butylamine (2.7 g.), benzylamine (2.5 g.) or *s*-butylamine (0.4 g.) and water (100 cc.) were boiled for forty minutes in a stream of carbon dioxide following the procedure used with the α-amino acids. At the end of the reaction, the contents of the receiver were warmed for some time and treated with 5 cc. of hydrochloric acid and then cooled. Acetaldehyde, butyraldehyde, benzaldehyde and methyl ethyl ketone were obtained in about 15% yield as the 2,4-dinitrophenylhydrazones. They were identified by the m. p. and the m. p. of mixtures with authentic samples.

Uramil was precipitated from the intense blue reaction mixture by cooling in ice. No reaction was detected when alloxantine was treated with *t*-butylamine.

Reaction of Hydrindantine with Amines.—Hydrindantine was treated with each of the amines listed in the preceding section, using 1.5-g. samples of hydrindantine following the same procedure as was used for testing alloxantine. The aldehyde corresponding to each of the amines again was isolated and identified. Treatment of the intensely violet reaction mixture with hydrochloric acid discharged the color, and precipitated violet bis-1,3-indandione; m. p. 298°, undepressed by mixing with authentic sample; yield 20%.

Summary

1. Structure of alloxantine is discussed and it is concluded that the evidence available favors the pinacol, rather than hemiacetal, formula.

2. Some new reactions of alloxantine and hydrindantine with amines and amino acids are described.

CAIRO, EGYPT RECEIVED MAY 31, 1949

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The Reaction of 1-Phenyl-1,3-butadiene with Hypochlorous Acid[1]

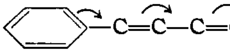
BY OLIVER GRUMMITT AND ROBERT M. VANCE[2]

As part of a study of the effect of the phenyl group on the behavior of a 1,3-butadiene side chain,[3] the addition of hypochlorous acid to 1-phenyl-1,3-butadiene has been investigated.

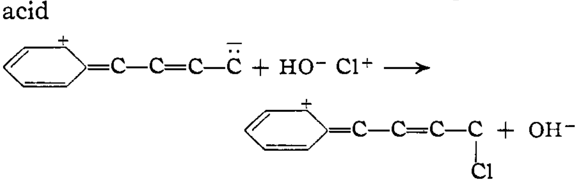
The reaction with one mole of acid can theoretically yield six structural isomers, since the 1,2, 3,4, and 1,4 modes of addition can each give a pair of isomers. In 1930 Muskat and Grimsley[4] reported that 3,4 addition gave 1-phenyl-3-hydroxy-4-chloro-1-butene (VII, Chart 2). Although the chlorohydrin was too unstable to isolate in pure form, it was ozonized to the expected benzaldehyde[5] and dehydrochlorinated to an epoxide whose structure was thought to be 1-phenyl-3,4-epoxy-1-butene. Further proof of 3,4 addition came from the dehydration of the crude chlorohydrin to 1-phenyl-4-chloro-1,3-butadiene (X), the structure of which was shown by (a) oxidation with silver oxide to γ-phenylisocrotonic acid (XIII), (b) independent synthesis by 3,4 addition of chlorine to phenylbutadiene followed by dehydrochlorination, and (c) the identity of the aniline derivatives, 1-phenyl-4-anilido-1,3-butadiene, made from the 4-chloro compounds obtained from the chlorohydrin and the dichloride.

Thus the 3,4 addition of hypochlorous acid to phenylbutadiene was generally accepted until 1937 when Abragam and Deux[6] reported only 1,2 addition. Again the crude chlorohydrin resisted purification but dehydrochlorination yielded 1-phenyl-1,2-epoxy-3-butene (III), based on (a) hydrolysis of the epoxide to a glycol, 1-phenyl-1,2-dihydroxy-3-butene (V), (b) hydrogenation to 1-phenyl-1-butanol, and (c) catalytic isomerization to α-phenylcrotonaldehyde. Whether the chlorohydrin had the 1-hydroxy-2-chloro- (I) or the 1-chloro-2-hydroxy structure (II), or was a mixture, was not established.

Because the electronic mechanism for this addition reaction points clearly to 1,4 and 3,4 addition, it seemed desirable to explore this reaction further. On theoretical grounds the activation of the butadiene side chain in the presence of a polar reagent involves a displacement of electrons out of the ring



The anionic terminal carbon atom reacts with the positively charged chlorine from hypochlorous acid



As a resonance hybrid, the positive charge in this activated intermediate would be distributed to the ortho and para carbon atoms in the ring but mostly to the first and third carbon atoms of the

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[1] Presented before the Division of Organic Chemistry at the San Francisco meeting of the American Chemical Society, April 31, 1949.

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[3] Grummitt and Becker, THIS JOURNAL, **70**, 149 (1948).

[4] Muskat and Grimsley, *ibid.*, **52**, 1574 (1930); **55**, 3762 (1933); Muskat and Huggins, **51**, 2496 (1929).

[5] This is not incontrovertible evidence for 3,4 addition because a 1,2 or 1,4 chlorohydrin, because of the allylic alcohol structure, might dehydrate very readily to re-establish the double bond adjacent to the ring and thus be oxidized to benzaldehyde.

[6] Abragam and Deux, *Compt. rend.*, **205**, 285 (1937).

side chain. Thus the addition of the anionic hydroxyl would give the 1,4 or 3,4 adduct.[7] This mechanism is supported by the fact that most additions to 1-phenyl-1,3-butadiene are 3,4[3] and by the principle of vinylogy.[8] Styrene adds hypochlorous acid normally[9] and phenylbutadiene is a vinylog of styrene.[9a]

Preliminary experiments showed that the important reaction variables are reactant ratio, temperature, and the method of preparing the hypochlorous acid. A slight molar excess of acid, temperatures of 0–10° in order to minimize polymerization of the phenylbutadiene, and hypochlorous acid from calcium hypochlorite and carbon dioxide[10] are, briefly, the conditions found to be most favorable for monochlorohydrin formation.

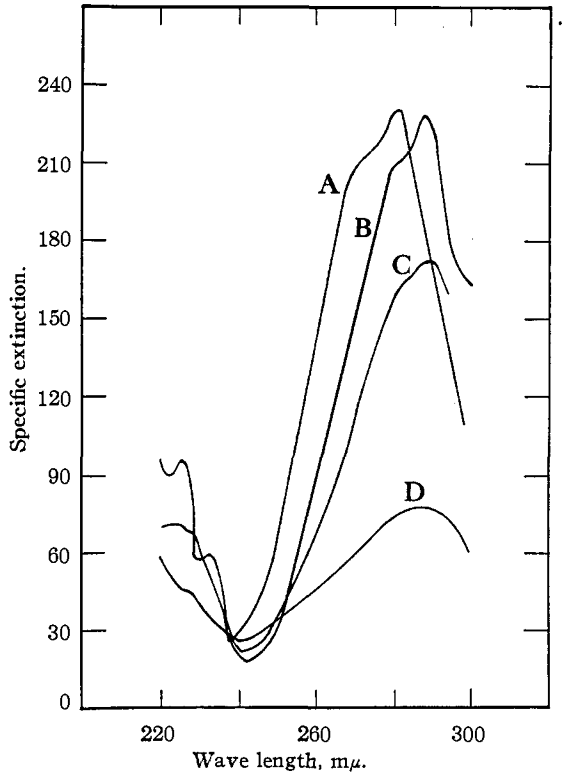

Fig. 1.—Ultraviolet absorption spectra of: A, 1-phenyl-1,3-butadiene; B, solid 1-phenyl-4-chlorobutadiene; C, liquid 1-phenyl-4-chlorobutadiene; D, crude phenylbutadiene chlorohydrin.

As previously reported,[4,6] the chlorohydrin was too unstable to allow separation from unreacted and polymerized phenylbutadiene and from dichlorohydrin. Even high vacuum distillation dehydrated the chlorohydrin to a phenylchlorobutadiene. Solvent extraction gave only a partial purification. Reduction of the side chain to obtain a more stable saturated chlorohydrin caused hydrogenolysis of the chlorine.

It was necessary therefore to characterize the crude chlorohydrin by its derivatives. By distillation at moderate vacuum the crude product was completely dehydrated to give about a 50% yield of a colorless liquid whose analysis and molecular weight corresponded to a phenylchlorobutadiene, C_6H_5-C_4H_4Cl. The presence of two conjugated double bonds in the side chain was shown by the formation of a tetrabromo derivative (XI) and by ultraviolet absorption curves (Fig. 1). The similarity in absorption between the phenylchlorobutadiene and phenylbutadiene and the low absorption of the chlorohydrin where conjugation is absent are apparent.

This liquid phenylchlorobutadiene was separated into liquid and solid fractions, and the latter melted 55–56° in agreement with the reported 1-phenyl-4-chloro-1,3-butadiene[4] (X). The liquid and solid products had the same empirical formula, yielded identical tetrabromo derivatives (XI), and underwent phenylation with phenylmagnesium iodide to *trans,trans*-1,4-diphenyl-1,3-butadiene (XII).[11] Neither substance reacted in a Diels–Alder addition with maleic anhydride, which is characteristic of 1,4 negatively substituted butadienes.[12] These properties suggested that the two substances were geometric isomers but the ultraviolet absorption spectra of the liquid showed no characteristic shift in wave length, as compared to the solid, but only a lower specific extinction at 288 mμ (Fig. 1). It seems more likely that the liquid product consists of the solid 1-phenyl-4-chloro-1,3-butadiene contaminated chiefly with a structural isomer in which the chlorine is at the 1 or 2 position (see subsequent discussion of 1,2 addition).

The oxidation by silver oxide of the phenylchlorobutadiene, liquid or solid, which had given γ-phenylisocrotonic acid[4] (XIII) could not be duplicated; instead, only a small yield (0.5%) of cinnamic acid (XIV) was obtained. When authentic γ-phenylisocrotonic acid was similarly oxidized, only a trace of cinnamic acid was found.[13] As evidence for the structure of the phenylchloro-

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[7] Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, Chapter 8.

[8] Fuson, *Chem. Rev.*, **16**, 1 (1935).

[9] Emerson, THIS JOURNAL, **67**, 516, 518 (1945).

[9a] Steric hindrance by the phenyl group as a factor in determining 1,2, 3,4, or 1,4 addition is not discussed here because the geometric isomerism of phenylbutadiene is just now being studied in this laboratory. It seems certain, however, that the compound used in this study is the *trans* isomer and, by analogy with the 1,4-addition of maleic anhydride (Robey, Morrell and Wiese, THIS JOURNAL, **63**, 627 (1941)) and of sulfur dioxide to piperylene (Craig, *ibid.*, **65**, 1006 (1943)), there may not be steric hindrance to addition at the 1-position.

[10] This reaction, $Ca(OCl)_2 + H_2O + CO_2 \rightarrow 2HOCl + CaCO_3$, is now widely used because of its convenience and the absence of chlorine and hydrochloric acid. For example, its use to make butadiene monochlorohydrin is described by Kadesch, THIS JOURNAL, **68**, 41 (1946).

[11] It was not expected that the vinyl chlorine would be reactive enough for this phenylation reaction. The behavior of the chlorine in this compound is being studied further.

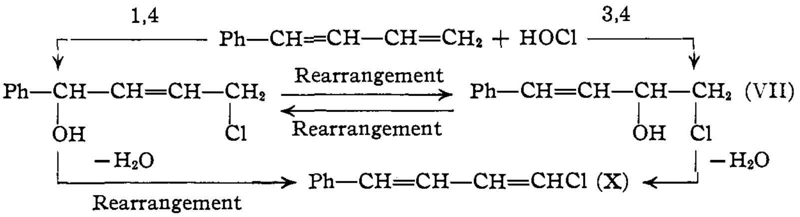
[12] Norton, *Chem. Revs.*, **31**, 319 (1942).

[13] Experimental conditions were not fully described in the earlier work and it is likely that we failed to duplicate them.

butadiene, the cinnamic acid is less significant because the chlorine atom might have been on either carbon atoms 3 or 4.

The evidence altogether points to the 1-phenyl-4-chloro structure for both the solid and liquid products, although the latter is not pure. Since the total yield is more than 50%, the major course of the addition of hypochlorous acid to phenylbutadiene is 3,4 although the possibility of 1,4 addition followed by rearrangement is not eliminated. Chart 1 shows both modes of addition and the theoretically possible rearrangement reactions.

CHART 1



The first step in investigating 1,2 addition was a repetition of the work of Abragam,[6,14] but the 1,2 epoxide was not found, and the only identifiable product was 1-phenyl-4-chlorobutadiene (X), a derivative of the 3,4 adduct. Since experimental details were lacking, the earlier work may not have been duplicated.

However, the 1,2 epoxide was obtained in about 14% yield by treatment of the crude chlorohydrin obtained by the calcium hypochlorite process with a suspension of potassium hydroxide in ether. By fractional distillation the epoxide could be separated from phenylbutadiene and 1-phenyl-4-chlorobutadiene. To confirm its structure as 1-phenyl-1,2-epoxy-3-butene (III) it was hydrolyzed to the known 1-phenyl-1,2-dihydroxy-3-butene (V) and catalytically reduced in the presence of Raney nickel to the known 1-phenyl-2-butanol (IV). The previously reported reduction had given the isomeric 1-butanol.[6] Since the 1,2-chlorohydrin was not isolated, the side chain structure may have been 1-chloro-2-hydroxy- (II) or 1-hydroxy-2-chloro- (I). The allylic and benzyl alcohol structures, respectively, of these adducts would allow ready dehydration and the phenylchlorobutadienes so formed may be present in the impure liquid phenylchlorobutadiene.

A careful repetition of the addition experiments of Muskat and Grimsley[4,15] confirmed the formation in low yield of the solid 1-phenyl-4-chloro-1,3-butadiene by distillation of the crude chlorohydrin, but the unidentified epoxide was shown to have the 1,2 structure. A liquid dichlorohydrin previously reported was successfully purified to give a solid melting 86–87°. The most probable structure, 1-phenyl-1,3-dihydroxy-2,4-dichlorobutane (VI), is based on the fact that 3,4 addition predominates and the assumption that the 1,2 double bond would then add hypochlorous acid as does styrene.[9]

An attempt to dehydrochlorinate the chlorohydrin to the epoxide with pyridine is noteworthy. The major product was not the epoxide but a crystalline, water soluble pyridinium salt of the chlorohydrin (VIII). Ozonolysis and oxidative decomposition of the ozonide gave benzoic acid and pyridine betaine hydrochloride (1-(carboxymethyl)-pyridinium chloride) (IX). Because the nitrogen in this product is attached to a methylene carbon, the chlorine atom displaced by the pyridine must have been on the terminal carbon atom of the chain. Thus the chlorohydrin had the 4-chloro structure but the hydroxy group might have been at positions one or three—*i. e.*, the chlorohydrin could have resulted from 1,4, 3,4, or both modes of addition.

Experimental

1-Phenyl-1,3-butadiene.—Prepared in about 80% yields by the action of methylmagnesium bromide on cinnamaldehyde and hydrolysis of the Grignard adduct in 30% sulfuric acid.[8] Phenyl-β-naphthylamine (0.1%) was added to the hydrocarbon as an anti-oxidant during storage at 0° and it was purified before use by vacuum distillation at 45–50° (1 mm.) or at 78–81° (8 mm.).

Addition of Hypochlorous Acid from Calcium Hypochlorite to Phenylbutadiene.—The following experiment is typical of numerous experiments run at various reactant ratios, temperatures, times, etc. In a one-liter three-necked flask fitted with a stirrer, thermometer, dropping funnel, a gas addition T-tube, and a gas outlet tube was placed 600 ml. of water and 31.5 g. (0.154 mole based on 70% $Ca(OCl)_2$) of technical calcium hypochlorite (Columbia Chemical "Pittchlor"). The gas addition tube reached to the bottom of the flask and, because of solid which tended to clog the open end, it was fitted with a glass rod sealed at the top with a rubber slip joint so that the outlet could be kept open. The mixture was stirred vigorously and kept at 0–3° while 40 g. (0.31 mole) of phenylbutadiene was added dropwise during one hour. At the same time carbon dioxide was bubbled through at the rate of 4 g./hr. as measured by a differential pressure flowmeter. When all of hypochlorous acid had been consumed, as shown by testing a portion of the reaction mixture for oxidizing action with aqueous potassium iodide, the mixture was filtered from calcium carbonate, the filtrate saturated with salt and extracted four times with 100-ml. portions of ether. The combined ether extracts were washed with water to remove chloride ions, dried overnight with 25 g. of Drierite, and the ether evaporated to give 50 g., 90% calculated as monochlorohydrin.

Addition of Hypochlorous Acid to Phenylbutadiene (Muskat).[4]—Our interpretation of this experiment was as follows: hypochlorous acid was made by bubbling chlorine into a stirred mixture of 500 ml. of water and 108 g. of mercuric oxide at 0° until the orange color disappeared. The solution was decanted and distilled from an all-glass apparatus. Small bits of Dry Ice were added at intervals to the distillate to cool it and to sweep out dissolved chlorine. An aliquot of the distillate was analyzed for hypochlorous acid by adding it to excess potassium iodide and hypochloric acid and titrating the iodine with standard thiosulfate. A 4% solution containing 0.31 mole of acid

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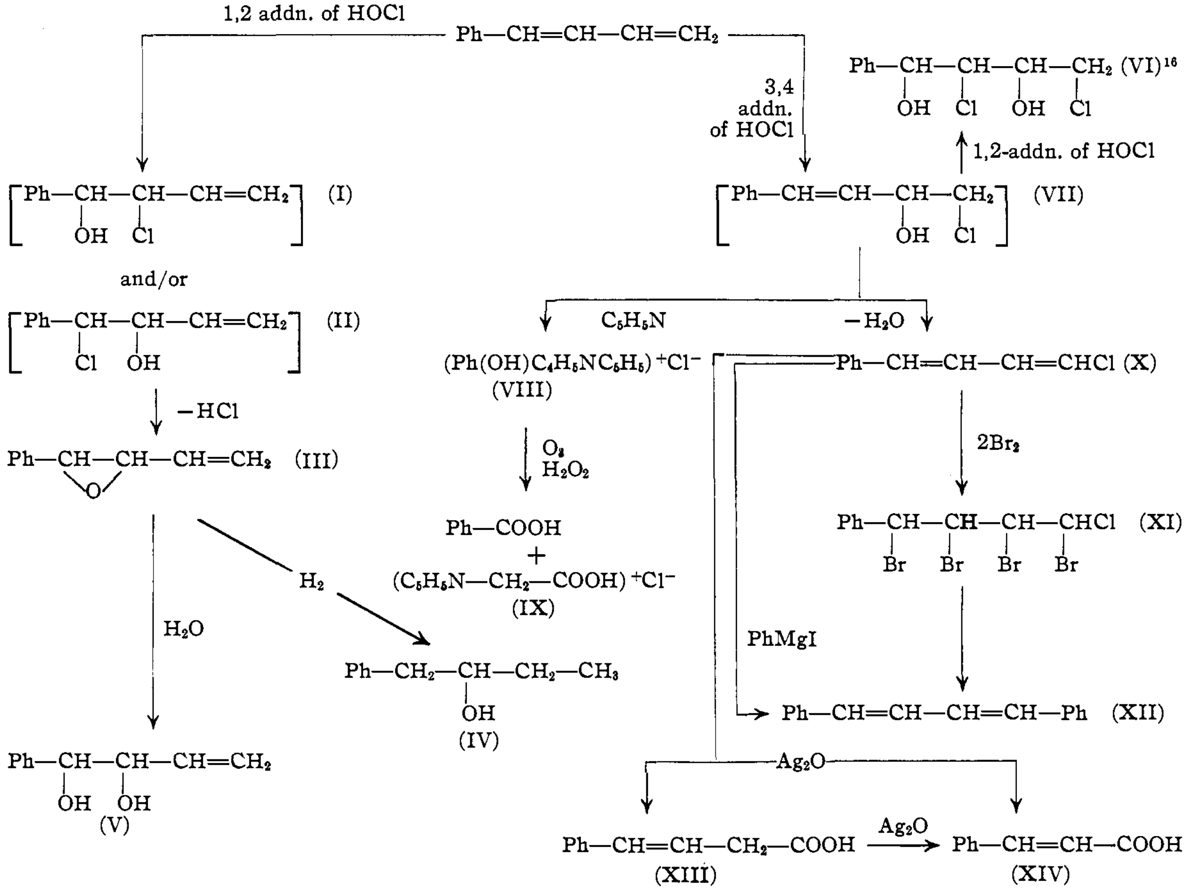
[14] Hypochlorous acid was made in this study by the action of chlorine on dilute acetic acid.

[15] Hypochlorous acid was made in this study by the action of mercuric oxide on chlorine water followed by distillation.

CHART 2



was allowed to react with 40 g. (0.31 mole) of phenylbutadiene at 0–5°. The product was isolated as described above. The yield of crude chlorohydrin was 52 g., 92% calculated as monochlorohydrin.

Addition of Hypochlorous Acid to Phenylbutadiene (Abragam).[5]—Our interpretation of this experiment was as follows: chlorine was added to a solution of 20 ml. of glacial acetic acid in 250 ml. of water cooled to 0° until 14 g. had dissolved. Titration showed that the solution contained about 0.17 mole of hypochlorous acid. This was added as rapidly as possible to 40 g. (0.31 mole) of phenylbutadiene while stirring and cooling to 10° or lower. The crude chlorohydrin was isolated as before.

Attempted Purification of the Monochlorohydrin.—Since the chlorohydrin should be less soluble in petroleum ether than the unreacted and polymerized phenylbutadiene, extraction was tried by dissolving 42 g. of crude chlorohydrin in 100 ml. of petroleum ether (b. p. 60–70°), cooling to −50°, separating the lower layer, and removing dissolved solvent from it by vacuum stripping. This yielded 34 g. of product whose hydroxyl content[17] was 6.6% and chlorine content 20.7%.[18] The extracted portion consisted of 27 g., 2.6% hydroxyl, 17.2% chlorine. These values, compared with the calculated values for phenylbutadiene chlorohydrin, 9.3% hydroxyl, 19.4% chlorine, show that the insoluble portion was richer in chlorohydrin than the soluble. Unfortunately further extractions with petroleum ether did not concentrate the chlorohydrin.

Vacuum distillation of the crude chlorohydrin at 0.1 mm. from an alembic flask gave no clear-cut fractions. Analysis of various samples of distillate showed hydroxyl contents of only 5–6%, indicating that no separation was being made and the probability that dehydration was occurring. Similar results were obtained by distillation of the petroleum ether insoluble portion described above.

Attempted Reduction of the Monochlorohydrin.—Because distillation indicated instability of the product, reduction of the double bond in the side chain was tried to obtain a more stable saturated monochlorohydrin. When an ether solution of the crude chlorohydrin was reduced in the presence of 10% palladium on charcoal at about 50 pounds pressure in a Parr low pressure hydrogenator, the solution contained hydrogen chloride equivalent to 71% of the chlorine present in the sample taken, and distillation yielded some *n*-butylbenzene (b. p. 23–27° (1 mm.)) (identified by boiling point and refractive index), which had formed by complete hydrogenation and hydrogenolysis of the side chain. At 74–85° (1 mm.) a small amount of solid melting 86–87° after crystallization from petroleum ether was obtained. Analysis indicated a phenylbutadiene dichlorohydrin (VI).

Anal. Calcd. for $C_{10}H_{12}Cl_2O_2$: Cl, 30.2; OH, 14.5. Found: Cl, 31.4; OH, 13.4.

1-Phenyl-4-chloro-1,3-butadiene (X).—When the crude phenylbutadiene chlorohydrin is freshly prepared it shows a broad absorption maximum at 280–290 mμ, suggesting that at least some dehydration to the conjugated phenyl-

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[16] The structure of this compound was not established.

[17] The active hydrogen analysis of Zerewitinoff, *Z. anal. Chem.*, **50**, 680 (1911), was used throughout this work. The acetic anhydride–pyridine analysis for hydroxyl groups (Freed and Wynne, *Ind. Eng. Chem., Anal. Ed.*, **8**, 278 (1936)) gave dark solutions which were not readily titratable.

[18] The method of Umhoefer, *Ind. Eng. Chem., Anal. Ed.*, **15**, 383 (1943), was used throughout this work.

chlorobutadiene has occurred (see Fig. 1). This dehydration is greatly accelerated by vacuum distilling the chlorohydrin at 5 mm. pressure, collecting a first fraction up to 100°, which is largely recovered phenylbutadiene, and a 100–105° liquid fraction which is phenylchlorobutadiene. Yields range from 25–50% by either the calcium hypochlorite or the Muskat method. The residue contains polymerized phenylbutadiene, dichlorohydrin, and probably other compounds. In one experiment benzaldehyde was isolated from the first cut and identified by its semicarbazone, m. p. 215–217°, and mixed melting point of 215–217° with a sample of authentic benzaldehyde semicarbazone. Presumably benzaldehyde had formed by oxidation of the phenylbutadiene or its adducts with hypochlorous acid as the oxidizing agent.

The liquid phenylchlorobutadiene fraction was purified by distillation at 78–82° (1 mm.); $n^{25}D$ 1.6283.

Anal. Calcd. for $C_{10}H_9Cl$: Cl, 21.6; mol. wt., 164.5. Found: Cl, 21.6; mol. wt. (f. p. in benzene), 160.5.

Cooling at 0° caused this liquid to crystallize partially. Separation and purification of the solid by crystallization from ethanol–water gave a colorless substance melting 55–56°.

Anal. Calcd. for $C_{10}H_9Cl$: Cl, 21.6; mol. wt., 164.5. Found: Cl, 21.6; mol. wt. (f. p. in benzene), 161.5.

Muskat reported a melting point of 52° for the 1-phenyl-4-chloro derivative.[4] Only about 15% of the liquid could be obtained as the solid. Chlorine analysis of the remaining liquid showed 21.6%. The refractive index of the solid at 55° was 1.623, of the liquid at 55°, 1.605.

The solid is not stable even at 0°. Hydrogen chloride is formed, a green color develops, and after several weeks the chlorine content had dropped to 15.1%.

A Diels–Alder reaction with maleic anhydride run in refluxing benzene in the usual way allowed most of the phenylchlorobutadiene to be recovered.

Catalytic hydrogenation at 50 lb. pressure of an ether solution with 10% palladium on charcoal liberated hydrogen chloride.

Oxidation of 1-Phenyl-4-chloro-1,3-butadiene.—The attempt to obtain γ-phenylisocrotonic acid (XIII)[4] by silver oxide oxidation was run as follows. A solution of 10% sodium hydroxide was added dropwise to 3.0 g. of silver nitrate dissolved in 14 ml. of water and the precipitated silver oxide filtered and washed with water. It was suspended by stirring in 100 ml. of water, 0.2 g. of solid phenylchlorobutadiene added, and the mixture was stirred and heated for twelve hours at 100°. After acidifying, filtering, washing the precipitate with ether and extracting the filtrate with ether, the combined ether extracts were extracted with 5% sodium carbonate solution, this solution was acidified and in turn extracted with ether. This extract yielded about 0.01 g. (0.5% yield) of solid melting 126–129° which in a mixed melting point with authentic cinnamic acid (m. p. 132–133°) melted 126–129°. The unknown and the authentic cinnamic acids gave *p*-bromophenacyl derivatives melting 141.5–142.5° and 144–145°, respectively. The mixed melting point was 142.5–144°.

An oxidation of authentic γ-phenylisocrotonic acid (m. p. 85–88°), made from sodium succinate, benzaldehyde, and acetic anhydride[19] also gave a very small yield of cinnamic acid (XIV).

1-Phenyl-4-chloro-1,2,3,4-tetrabromobutane (XI).—Both the solid and liquid phenylchlorobutadienes were allowed to react in carbon tetrachloride solution in the dark and at 0° with slightly more than two moles of bromine. Crystallization from ethanol gave the tetrabromides: m. p. 145–146° from the solid, 142–145° from the liquid. A mixed melting point was 141–145°.

Anal. Calcd. for $C_{10}H_9Br_4Cl$: Cl and Br, 73.3. Found: Cl and Br, 74.3.

***trans,trans*-1,4-Diphenyl-1,3-butadiene (XII).**—To phenylmagnesium iodide made from 0.3 g. (0.012 atom) of magnesium, 2.5 g. (0.012 mole) of iodobenzene, and 3 ml. of di-*n*-butyl ether was added a solution of 2.0 g. (0.012 mole) of liquid phenylchlorobutadiene in butyl ether. Isolating the product in the usual way and crystallizing several times from ethanol gave 0.4 g. (12%) melting 149–151°. An authentic sample prepared from phenylacetic acid and cinnamaldehyde[20] melted 149–151° and a mixed melting point showed no depression. The solid phenylchlorobutadiene, m. p. 50–53°, also gave this diphenylbutadiene but in very small yield.

Dehydrochlorination of Phenylbutadiene Chlorohydrin.—Crude chlorohydrins made by the calcium hypochlorite method, according to Muskat,[4] and according to Abragam,[6] were run under various conditions. As dehydrochlorinating agents the following were tried: (1) a suspension of powdered potassium hydroxide in mineral oil heated and stirred at 140–150° (1 mm.) while the chlorohydrin was added dropwise and the distillate collected; (2) twenty per cent. aqueous potassium hydroxide to which chlorohydrin was added dropwise, the mixture stirred at room temperature, and aliquots analyzed by the Volhard method until no more chloride ion formed; (3) a slurry of potassium hydroxide in *n*-butanol–toluene made by adding a concentrated solution of 25 g. of aqueous potassium hydroxide to 120 ml. of toluene and 7 ml. of *n*-butanol, stirring and distilling with a Dean–Stark receiver until no more water came over[21]; 47 g. of chlorohydrin was added to the cold mixture over 45 minutes and after ten minutes the product was isolated by addition of water, ether extraction, etc.; (4) a suspension of finely powdered potassium hydroxide in absolute ether, 25 g. to 200 ml., with which 40 g. of chlorohydrin was allowed to react for two hours, first at 0° and then at room temperature; washing with water and distillation of the ether solution followed; (5) a pyridine–chlorohydrin solution at room temperature from which aliquots were taken for Volhard chloride analysis.

Although each of these methods was not exhaustively tried, the potassium hydroxide–ether suspension (3) gave the best yields. Distillation of the ether solution gave fractions at 45–75° (1 mm.) and at 75–85° (1 mm.). The first fraction consisted of phenylbutadiene and the phenylbutadiene epoxide (III) and the second was the liquid phenylchlorobutadiene. Muskat reported a boiling point of 94° (6 mm.) for the epoxide and Abragam reported 99–101° (6 mm.). By vacuum fractional distillation of the first fraction through a glass helix-packed column of 12 plates efficiency the higher boiling epoxide could be separated; phenylbutadiene, identified as its maleic anhydride adduct,[22] was collected at 30–33° (1 mm.) and the epoxide at 37–44° (1 mm.). The maximum yield of epoxide based on phenylbutadiene was 14%. For the characterization reactions described below the impure epoxide was used because the derivative, in the case of the hydrogenation and hydrolysis reactions, was much higher boiling than the phenylbutadiene.

Analysis of the pure epoxide by addition of hydrogen chloride, the oxirane analysis,[23] indicated an oxygen content of about 5% compared to the calculated of 10.95%. This method, however, has been shown to be unreliable for analogous compounds such as styrene oxide.[24]

The attempted dehydrochlorination with pyridine was run with a solution of 40 g. of chlorohydrin and 200 ml. of pyridine at room temperature for fifteen hours when a chloride analysis showed that the reaction had proceeded 23% of the theoretical extent, based on the assumption that the chlorohydrin was pure. A crystalline precipitate was separated, purified by crystallizations from dioxane–ethanol until the melting point was 175–176.5°. The

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(19) Fittig and Jayne, *Ann.*, **216**, 98 (1882). This synthesis is greatly improved if the intermediate γ-phenylparaconic acid is decomposed in a sublimation apparatus heated carefully by an open flame. This will give an almost quantitative yield of the crotonic acid.

(20) "Org. Syntheses," Coll. Vol. II, 229 (1943).

(21) Smith, U. S. Patent 2,385,547, September 25, 1945.

(22) Alder and Rickert, *Ber.*, **71B**, 379 (1938).

(23) Nicolet and Poulter, THIS JOURNAL, **52**, 1186 (1930).

(24) Swern, Findley, Billen and Scanlan, *Ind. Eng. Chem., Anal. Ed.*, **19**, 414 (1947).

salt-like nature of the compound was shown by its solubility in water and 95% ethanol, insolubility in ether. A chloride analysis was run by adding weighed samples to water and following the usual Volhard procedure. The result corresponded to a pyridinium salt of the phenylbutadiene chlorohydrin (VIII).

Anal. Calcd. for $C_{15}H_{16}NOCl$: Cl, 13.6. Found: Cl, 13.7.

Ozonolysis of 1 g. of the salt in 50 ml. of water and decomposition of the ozonide by refluxing with 2 ml. of 30% hydrogen peroxide overnight gave an ether-soluble product and a water-soluble product. The ether extract yielded 0.2 g. of crystalline solid which was converted to the *p*-bromophenacyl derivative in the usual way.[25] This melted 112–114°, the authentic *p*-bromophenacyl ester of benzoic acid melted 119–120°, and a mixed melting point gave 116–118°. Evaporation of the water solution gave a crystalline solid which melted and decomposed at about 195°.[26] Analysis for chloride ion checked the empirical formula for pyridine–betaine hydrochloride, $[C_5H_5NCH_2COOH]Cl$ (IX).

Anal. Calcd. for $C_7H_8O_2NCl$: Cl, 20.4. Found: Cl, 21.0.

Pyridine and 1-phenyl-4-chlorobutadiene showed no evidence of reaction after standing several days.

Reduction of 1-Phenyl-1,2-epoxy-3-butene (III).—A solution of 7 g. of epoxide in absolute ether with 0.5 g. of 10% palladium on charcoal was hydrogenated in the Parr low pressure apparatus in the usual way. Distillation yielded 5.3 g. of liquid boiling 60–65° (1 mm.). The α-naphthylurethan[27] melted 101–104°, the same derivative of 1-phenyl-2-butanol (IV) melted 101–105°, and a mixed melting point gave no depression. The phenylurethans[27] melted 79–80° and 78–81°, respectively, and also showed no depression in a mixed melting point. The 1-phenyl-2-butanol was made by the Grignard reaction of ethyl bromide and phenylacetaldehyde in 70% yield, b. p. 61–66° (1 mm.).[28]

Because Abragam had obtained the isomeric 1-phenyl-1-butanol by reduction of the epoxide, this alcohol was also made. Its phenylurethan was a liquid at room temperature and its α-naphthylurethan melted 106–108°. A mixed melting point with the same derivative from the epoxide reduction was 86–94°. The 1-phenyl-1-butanol was obtained through the Grignard reaction of *n*-propyl bromide and benzaldehyde in 53% yield; b. p. 90–95° (1 mm.).[28]

Hydrolysis of 1-Phenyl-1,2-epoxy-3-butene.—Six grams of the epoxide reacted with 35 ml. of 1% hydrochloric acid at 100° for 3 hours, the solution was extracted with ether, and the ether solution distilled to give 3.2 g. boiling 107–111° (1 mm.). Crystallization from benzene gave 2.1 g. melting 40–42°. The reported melting point of the glycol 1 phenyl-1,2-dihydroxy-3-butene (V) is 43°.[29]

Phenylbutadiene Dichlorohydrin (VI).—This compound was first isolated from the higher boiling fractions of the reduction products from the monochlorohydrin as a solid melting 86–87°. One experiment with 2.0 moles of hypochlorous acid from calcium hypochlorite and 1.0 mole of phenylbutadiene run as for the monochlorohydrin gave only a small yield, less than 1%, of the dichlorohydrin, m. p. 86–87°. No attempt was made to determine the structure of this compound.

Ultraviolet Absorption Spectra.—The measurements were made on 95% ethanol solutions of the compounds in 1-cm. quartz cells with a Beckman Model DU ultraviolet spectrophotometer.

Summary

Pure monochlorohydrins from the reaction of 1-phenyl-1,3-butadiene with hypochlorous acid could not be isolated. As reported earlier, the mode of addition is 1,2 and 3,4 but *both* reactions occur under the conditions used here and very probably under all conditions. The predominant mode of addition is 3,4, as shown by the relative yields of products derived from the chlorohydrins. The ratio of 3,4 to 1,2 addition is 3–4/1. This result fulfills the prediction from an electronic mechanism and shows again the generally greater reactivity of the 3,4 double bond compared to the 1,2 in 1-phenyl-1,3-butadiene.

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(25) Shriner and Fuson, "Identification of Organic Compounds," 3rd ed., John Wiley and Sons, New York, N. Y., 1948, p. 157.

(26) The same melting characteristics are described by von Gerichter for pyridine betaine hydrochloride made from monochloroacetic acid and pyridine (*Ber.*, **15**, 1251 (1882)).

(27) Reference 25, p. 163.

(28) Lagerev, *Trudy Uzbekskogo Gosudarst. Univ.*, **6**, 71 (1936); *C. A.*, **35**, 2119 (1941).

(29) Tiffeneau and Weill, *Compt. rend.*, **200**, 1217 (1935); Deux, *ibid.*, **211**, 441 (1940).

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Primary Hydroxyl Groups in Hydrolyzed Cellulose Acetate[1]

BY CARL J. MALM, LEO J. TANGHE AND BARBARA C. LAIRD

The tritylation of cellulose has been carefully studied[2] and it has been shown that the trityl group in the "mono-trityl ether" is predominantly in the primary or number 6 position. The tritylation of a single sample of cellulose acetate has been reported.[3] About one third of the hydroxyl groups reacted.

Since the tosylation and iodination method did not give cleancut results[4] in the determination of primary hydroxyl in cellulose acetate, tritylation was used to determine whether the amount of primary hydroxyl in a sample of cellulose acetate depends on its method of preparation. The amount of trityl introduced under standardized conditions was taken as a measure of the amount of primary hydroxyl present.

Tritylation Conditions.—Trityl ethers were prepared from cellulose acetate by reaction with trityl chloride in the presence of pyridine. Since

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(1) Presented before the Division of Cellulose Chemistry at the 116th Meeting of the American Chemical Society, Atlantic City, N. J., September 22, 1949.

(2) (a) W. M. Hearon, G. D. Hiatt and C. R. Fordyce, THIS JOURNAL, **65**, 2449 (1943); (b) J. Honeyman, *J. Chem. Soc.*, 168 (1947).

(3) I. Sakurada and T. Kitabatake, *J. Soc. Chem. Ind.*, Japan, Supplemental Binding, **37**, 604B (1934).

(4) C. J. Malm, L. J. Tanghe and B. C. Laird, THIS JOURNAL, **70**, 2740 (1948).