

Summary

1. The structural relationship of allenes and diaryl carbodiimides has been pointed out and a method for proving the asymmetry of the carbodiimide proposed.

2. Experiments on the preparation of various carbodiimides have been described and the difficulties in the study of these substances pointed out.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY AND THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

INVESTIGATIONS ON THE STEREOISOMERISM OF UNSATURATED COMPOUNDS. I. THE COMPOSITION OF CROTONALDEHYDE

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The program of research undertaken includes a study of the physical and chemical properties of a series of aliphatic hydrocarbons containing conjugated systems of double bonds. Since these compounds may occur in several stereoisomeric forms, it is necessary to isolate the individual isomers in order to obtain reliable physico-chemical measurements. Such procedure will enable one to determine the influence of the configuration of the individual double bonds on the physical and chemical properties of these hydrocarbons.

The keynote in this work is purity of materials. For this reason the separation of isomeric mixtures by fractional distillation was avoided because of the inherent difficulties.² Instead of this, the author is studying methods of synthesis which will lead to the production of pure isomers, the first of which is *trans,trans,trans*-dimethylhexatriene. To do this, one must know the configuration of the starting materials as well as the intermediate compounds.

One of the starting materials investigated is the so-called crotonaldehyde which is commonly obtained from aldol. This material might be a mixture of *cis*- and *trans*-crotonaldehydes and vinyl acetaldehyde. If this is the case the resulting hexatriene might be a mixture of as many as eight different isomeric hydrocarbons. Therefore a quantitative study of ordinary crotonaldehyde³ was undertaken by several different methods. The first re-

¹ The experimental part of this work was completed while the author was a National Research Fellow in Chemistry at Stanford University. This paper was presented at the Pasadena meeting of the American Association for the Advancement of Science, June 19, 1931. Original manuscript received June 29, 1931.

² Lucas, Dillon and Young, *THIS JOURNAL*, **52**, 1949 (1930).

³ Commercial crotonaldehyde was obtained from one manufacturer in order to ensure an unlimited supply of material of constant composition.

sults are presented in this article, namely, oxidation with oxygen and with silver oxide.

Previous Investigations on the Composition of Crotonaldehyde by Oxidation.—Several investigators⁴ have reported the oxidation of crotonaldehyde preparations but the composition of none of these has been conclusively established. Kekulé^{4a} and Charon^{4b} obtained *trans*-crotonic acid by oxidation with air or oxygen and concluded that their material was *trans*-crotonaldehyde. Duchesne and Délépine^{4c} recovered in addition some acetic acid and Kaufler,^{4f} using a more elaborate method, isolated still another product, *cis*-crotonic acid in 6% yields. Unfortunately neither the source of the aldehyde nor the method of oxidation was adequately described by Kaufler.

Kekulé,^{4a} Charon^{4b} and Délépine and Bonnet^{4d} used silver oxide in the oxidation of crotonaldehyde. Of these, only Charon carefully avoided stereomutation of the materials, and indicated that his product was pure *trans*-crotonic acid. Inasmuch as he extracted this product from the acidified reaction mixture with ether, it is quite possible that appreciable quantities of the extremely soluble *cis*-crotonic acid may have been lost in the mother liquor. In view of the uncertainty of this question we have attempted to ascertain whether or not *cis*-crotonic acid is actually a product of the oxidation of crotonaldehyde.

Any chemical reactions to which crotonaldehyde is submitted must be performed under carefully controlled conditions in order to avoid stereomutation either in the aldehyde or in its reaction products. Stereomutation of *cis* isomers readily occurs in the case of *cis*-crotonic acid and its homologs,^{5,6} especially if traces of catalysts are present, and equilibria involving stereomutation of *trans* isomers have been observed at temperatures as low as 100°. ^{7,8} Another possible rearrangement, shifting of the double bond from the α, β to the less stable β, γ position is very unlikely, since there is no substitution in the γ position.⁹

Method of this Investigation.—In the oxidation of crotonaldehyde the experiments were designed to account quantitatively for all of the crotonic acids formed during the oxidation and to avoid conditions favoring molecular rearrangements during the oxidation process and subsequent treatment.

For comparison two series of experiments were run: one on the commer-

⁴ (a) Kekulé, *Ann.*, **162**, 100 (1872); (b) Charon, *Ann. chim. phys.*, [7] **17**, 216 (1897); (c) Délépine, *ibid.*, [8] **16**, 136 (1909); (d) Délépine and Bonnet, *Compt. rend.*, **149**, 40 (1909); *Bull. soc. chim.*, [4] **5**, 882 (1909); (e) Duchesne and Délépine, *ibid.*, [4] **35**, 1311 (1924); (f) Kaufler, *Monatsh.*, **53-54**, 119 (1929).

⁵ Wislicenus, *Ann.*, **248**, 341 (1888); *Chem. Zentr.*, II, 259 (1897).

⁶ Blaise, *Ann. chim. phys.*, [8] **11**, 116 (1907).

⁷ Morrel and Hanson, *J. Chem. Soc.*, **85**, 1520 (1904).

⁸ Skau and Saxton, *THIS JOURNAL*, **52**, 335 (1930).

⁹ "Annual Reports on the Progress of Chemistry," **24**, 111 (1927).

cial crotonaldehyde, the other, on *trans*-crotonaldehyde. The *trans*-crotonaldehyde was prepared by treating the original aldehyde with hydrogen chloride and strong sunlight for several hours to transform any possible *cis* isomer which may have been originally present. It is well known that hydrochloric acid catalyzes this change in closely related substances.^{5,6}

The original and sunlight-irradiated aldehydes were separately oxidized by two different reagents, gaseous oxygen and alkaline silver oxide. The content of *cis*- and *trans*-crotonic acids in the oxidation mixtures from both series of experiments was estimated by fractional crystallization of their sodium salts.¹⁰ The different salt fractions were analyzed for total crotonate content by titration with bromine water. Although Buckwalter and Wagner¹¹ reported that crotonic acid is not brominated readily, we have found that the sodium salt is rapidly and quantitatively brominated in neutral solution.

Discussion of Results.—There was excellent agreement between the results on the commercial and sunlight-irradiated aldehydes with both oxygen and silver oxide. No *cis*-crotonic acid was isolated in any of the controlled experiments, though as much as 5% was isolated from the gaseous oxidation of both aldehydes when the temperature of the reaction mixture was *not controlled*. It was therefore concluded that the aldehyde under investigation was free from the *cis* isomer and that *cis*-crotonic acid is not produced during the oxidation of crotonaldehyde under *controlled* conditions. It is indeed unfortunate that Kaufler^{4f} did not discuss his method of oxidation, since this part of the work requires the most careful regulation. His *cis*-crotonic acid may readily be accounted for if the reaction temperature were not controlled.

Experimental Procedure

Purification of Crotonaldehyde.—The commercial crotonaldehyde obtained from the Niacet Chemical Corporation was purified by two distillations through an 80-centimeter Vigreux column: b. p. of distillate, 101.3–102.0°; n_D^{20} 1.4356.

Preparation of Trans-Crotonaldehyde.—Commercial crotonaldehyde was placed in a quartz flask with a few cubic centimeters of concentrated hydrochloric acid and exposed to strong sunlight for several hours to remove any *cis*-crotonaldehyde originally present. The reaction mixture was then twice distilled through an 80-cm. Vigreux column: b. p. 101.3–101.7; n_D^{20} 1.4362.

The Oxidation of Crotonaldehyde with Gaseous Oxygen.—The gaseous oxidations of crotonaldehyde were carried out by shaking the material in a closed system in order to follow the oxygen absorption quantitatively. The temperature of the reaction mixture was kept below 30°, since in preliminary experiments the reaction temperature often reached 50–90° in ten or fifteen minutes, accompanied by the formation of some *cis*-crotonic acid and large quantities of resin. When oxygen was no longer absorbed the unchanged crotonaldehyde was distilled from the reaction mixture at 70-mm. pressure

¹⁰ This method of analysis has been used by Wislicenus⁵; Kaufler^{4f}; Auwers and Wissebach, *Ber.*, **56**, 715 (1923); and Braun, *THIS JOURNAL*, **51**, 228 (1929).

¹¹ Buckwalter and Wagner, *ibid.*, **52**, 5248 (1930).

and again shaken in the absorption apparatus. The products from both oxidations were then combined and separated into four fractions; fraction 1 (b. p. (18 mm.) 31–45°), acetic acid; fraction 2 (b. p. (15 mm.) 45–83°); fraction 3 (b. p. (15 mm.) 83–87°); and an acid-resin residue. The boiling point rose from 45 to 83° in less than thirty seconds and only a few drops of liquid distilled. This indicated the absence of *cis*-crotonic acid and vinylacetic acid. As a further proof for the absence of these substances the crotonic acid, fraction 3, was converted into its sodium salt by neutralization with sodium ethylate and analyzed according to Kaufer.^{4f} If the temperature of the reaction mixture was not controlled during the oxidation process, both fraction 2 and fraction 3 contained detectable quantities of *cis*-crotonic acid. Typical results of the experiments with gaseous oxygen are shown in Table I.

The Oxidation of Crotonaldehyde with Silver Oxide.—To make sure that the gaseous method gave dependable results, an entirely different process was resorted to, namely, oxidation with silver oxide. This reagent was more satisfactory than oxygen since the reaction products were free from resin acids and could be readily isolated without danger of rearrangements.^{4b} The reaction was performed as follows.

The aldehyde was shaken vigorously with a water suspension of silver oxide at 15–20°. The reaction was complete in six hours. Through metathesis, the silver salt was converted into the sodium salt by shaking with sodium carbonate or sodium hydroxide. The solution was filtered and the filtrate neutralized with 6 *N* sulfuric acid. After the crotonate content of the solution had been determined, the water was removed at 27° under reduced pressure. The residue was then analyzed for *cis*- and *trans*-crotonic acids by Kaufer's method.^{4f} All of the crotonate in the solution was thus accounted for as the *trans* isomer. Typical experiments on the original and irradiated aldehydes

TABLE I
THE FRACTIONAL EXTRACTION OF SODIUM CROTONATE RESIDUE OBTAINED FROM THE OXIDATION OF CROTONALDEHYDE

Expt. 1.	Original Aldehyde + Oxygen
Expt. 2.	Irradiated Aldehyde + Oxygen
Expt. 3.	Original Aldehyde + Silver Oxide
Expt. 4.	Irradiated Aldehyde + Silver Oxide
Expt. 5.	Irradiated Aldehyde + Oxygen (temperature uncontrolled)

		EXPERIMENT 1							
		1st Extn.		2d Extn.		3d Extn.			
		A	C	F	H				
Weight of salt extracted		56.4	3.2	1.7	1.0				
		700 cc.	100 cc.	20 cc.					
		alc.		alc.		alc.			
Weight of insoluble residue			B	D	G	H			
			52.9	1.6	0.7	1.0			
Sodium crotonate in residue			52.9	1.6	0.6	0.0			

		EXPERIMENT 2							
		1st Extn.		2d Extn.		3d Extn.			
		A	C	F	H				
Weight of salt extracted		52.5	3.3	1.6	0.8				
		700 cc.	100 cc.	20 cc.					
		alc.		alc.		alc.			
Weight of insoluble residue			B	D	G	H			
			48.9	1.7	0.8	0.8			
Sodium crotonate in residue			48.9	1.55	0.6	0.0			

TABLE I (Concluded)

		EXPERIMENT 3					
		1st Extn.		2d Extn.		3d Extn.	
Weight of salt extracted*		500 cc.	C 36.5	100 cc.	F 4.2	20 cc.	H 0.4
		alc.		alc.		alc.	
Weight of insoluble residue			B 60.6		D 24.2		G 3.7
Sodium crotonate in residue			↓ 39.4		↓ 16.3		↓ 0.4
							H 0.4
							↓ 0.11
		EXPERIMENT 4					
		1st Extn.		2d Extn.		3d Extn.	
Weight of salt extracted*		500 cc.	C 33.8	100 cc.	F 4.2	20 cc.	H 1.2
		alc.		alc.		alc.	
Weight of insoluble residue			B 46.3		D 23.3		G 3.0
Sodium crotonate in residue			↓ 34.8		↓ 21.0		↓ 1.96
							H 1.2
							↓ 0.17
		EXPERIMENT 5					
		1st Extn.		2d Extn.		3d Extn.	
Weight of salt extracted	A 55.1	700 cc.	C 6.0	100 cc.	F 4.9	20 cc.	H 4.1
		alc.		alc.		alc.	
Weight of insoluble residue			B 48.1		D 1.8		G 0.8
Sodium crotonate in residue			↓ 48.1		↓ 1.7		↓ 0.7
							H 4.1
							↓ 3.3

A is the weight of salt at the start of extraction process.

C, F, H are weights of salt dissolved in extractions 1, 2 and 3, respectively.

B, D, G are weights of salt undissolved in extractions 1, 2, 3, respectively.

* The weight of the crude salt was not determined in this case.

are listed in Table I. In all experiments the *cis*-sodium crotonate should be found in the last extract H. From the table it is seen that of the salt dissolved a negligible quantity reacts with bromine, except in experiment 5 where the reaction temperature was not controlled. Therefore if any *cis*-crotonic acid is formed on oxidation with silver oxide or oxygen it is formed in very small amount.

In conclusion the writer desires to express his appreciation of the kindly interest shown by members of the Chemistry Staff at Stanford University and at the Division of Plant Biology of the Carnegie Institution of Washington, located at Stanford, especially to Doctors H. A. Spoehr and J. H. C. Smith, who offered many helpful suggestions and criticisms.

Summary

The composition of crotonaldehyde has been investigated by oxidation with gaseous oxygen and alkaline silver oxide under conditions designed to

avoid molecular rearrangements. It was shown that "niacet" crotonaldehyde is the *trans* isomer by comparison with *trans*-crotonaldehyde prepared by treatment with hydrogen chloride and sunlight. Both aldehydes gave only *trans*-crotonic acid on oxidation under controlled conditions, but some *cis*-crotonic acid when the temperature was not controlled.

It was concluded that the *cis*-crotonic acid reported by Kaufler⁴ was probably formed from the *trans* isomer by stereomutation during the oxidation process.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

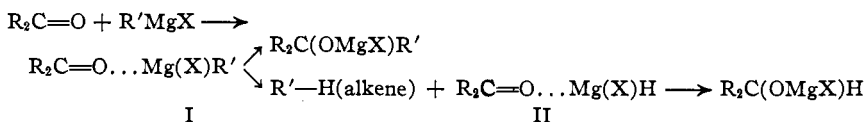
THE REDUCING ACTION OF THE GRIGNARD REAGENT.
II. COMPARISON WITH THE EASE OF REMOVAL OF
HYDROGEN BROMIDE FROM ALKYL BROMIDES AND WITH
THE AMOUNT OF DIALKYL MAGNESIUM IN THE GRIGNARD
REAGENT

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The theory proposed by Hess and Rheinboldt¹ to account for the reducing action of certain alkylmagnesium halides is that a primary addition product with the carbonyl compound is first formed and that this may either rearrange to give the normal addition product or may lose unsaturated hydrocarbon and then rearrange to give the reduction product.



Meisenheimer² proposed a similar mechanism except that the postulation of the intermediate compound II is omitted.

One might predict, if Hess' formulation represents the mechanism of the reaction, that for a series of alkylmagnesium halides the relative ease with which unsaturated hydrocarbon is lost from the complex $R_2CO \dots Mg(X)R'$ and hence the relative amount of reduction might be comparable with the relative ease with which alkenes are formed from alkyl halides. A rough evaluation of the relative ease with which pyridine reacts with alkyl bromides to form alkene and pyridine hydrobromide has been reported recently³ and it is the purpose of this paper to present data on the amount of reduction brought about by Grignard reagents from these same alkyl

¹ Hess and Rheinboldt, *Ber.*, **54**, 2043 (1921).

² Meisenheimer, *Ann.*, **442**, 180 (1925).

³ Noller and Dinsmore, *THIS JOURNAL*, **54**, 1025 (1932).