[A CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

Quantitative Hydrogenation at 100-300 Atmospheres

BY HOMER ADKINS

Suitable apparatus apparently has not yet been described for the quantitative measurement of the absorption of hydrogen by an organic compound over a catalyst at pressures above a few atmospheres. Such an apparatus would be useful for several purposes, *viz.*, the determination of the degree of unsaturation of a substance such as carotene; the determination of the amount of an unsaturated compound in a mixture, as for example in the estimation of the amount of a pyridine in the presence of a piperidine derivative; in the selection of optimum conditions for and the control of the hydrogenation of compounds available in quantities of only a few thousandths of a mole. An apparatus satisfactory for these purposes must have a small internal volume and be absolutely hydrogen tight at pressures up to 200 atmospheres and temperatures up to 250°. In addition it should be safe and simple, and as inexpensive as possible. Such a piece of equipment has been in use in this Laboratory for some time and its construction and use are described below.

The design of the bomb and assembly has been modified from that previously described[1] for the sake of economy of construction, and convenience in use, as well as to meet the necessity for a small internal volume in quantitative work. These changes involve first, the elimination of the liner and the use of a small bent copper tube to prevent the catalyst and liquid from entering the hydrogen line and gage; second, the location of the thermocouple well in the wall of the bomb instead of as a separate unit which entered the bomb cavity. These two changes have reduced the cost of a small outfit to less than one-half of that of the former type. The location of the thermocouple in the wall of the bomb also results in a more even temperature control of the contents of the bomb. Much more important, however, is the fact that the copper gasket is now so much smaller in diameter that it is more readily crushed and the possibility of leakage practically eliminated. These advantages have been utilized not only in a bomb for quantitative work, but also in one for hydrogenations involving up to 80 ml. of material, a capacity which is very useful in preparational work. This type of bomb may be used either with a spiral of steel tubing for the introduction of hydrogen while the bomb is in motion, or with the simpler and more inexpensive gage assembly described below.

The dimensions of the two bombs are given in Table I, a cross section of

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(1) Adkins, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 342 (1932). Unfortunately, mistakes were there made in the interconversion of inches and metric units, with respect to the thickness of the copper gasket (1.6 mm.), the internal chamber of the steel tubing (1.6 mm.), and the length of the spiral (4.3 m.).

one in Fig. 1 and a photograph of the assembled apparatus in Fig. 2. The gage assembly consists of the following parts: a hydraulic gage 3.5 inches in diameter calibrated to 5000 lb. per sq. in. (or 10,000 for pressures of 200–300 atmospheres) as supplied by the United States Gage Company, 44 Beaver Street, New York, is screwed against a copper gasket in a three-way superpressure needle valve supplied by the American Instrument Company, 774 Girard Street, Washington, D. C. The openings in this valve are so placed that when the valve is closed no gas pressure is exerted on the valve packing. A 7-cm. nipple of 6.3 × 1.6 mm. steel tubing with standard couplings is connected to the opening in the valve opposite the valve stem. One of the two hexagonal nuts on the couplings should be 2.3 instead of the usual 1 cm. in length.

TABLE I

DIMENSIONS OF BOMBS

		A		B	
		Inches	Cm.	Inches	Cm.
Bomb diameter	o. d.	2.12	5.40	2.31	5.88
	i. d.	0.75	1.90	1.31	3.34
Bomb length	o. d.	6.44	16.30	8.75	22.20
	i. d.	5.87	14.90	8.00	20.30
Thermocouple well	diam.	0.19	0.48	0.19	0.48
	depth	3.00	7.62	3.00	7.62
Bomb head	diam.	2.00	5.08	2.12	5.40
	thickness	0.50	1.27	0.50	1.27
Bomb head (boss)	diam.	.87	2.22	.87	2.22
	height	1.00	2.54	1.00	2.54
Channel in b. and b. h.	diam.	1.00	2.54	1.56	3.96
	depth	0.05	0.13	0.05	0.13
Gasket recess in b. h.[2]	depth	.15	.04	.15	.04
Bomb head cover	diam.	2.56	6.50	2.87	7.30
	height	2.62	6.66	2.75	7.00
Bomb head cover (recess)	diam.	2.03	5.13	2.15	5.45
	depth	1.87	4.76	2.00	5.08
Open. in b. h. cover for boss of b. h.	diam.	0.90	2.29	0.90	2.29
Threaded (8 per inch)	bomb	1.25	3.18	1.50	3.81
	b. h. c.	1.25	3.18	1.50	3.81
Copper gasket	o. d.	1.25	3.18	1.81	4.61
	i. d.	0.75	1.90	1.31	3.34
	thickness	.06	0.16	0.06	0.16
Brass thrust plate	o. d.	2.00	5.08	2.12	5.40
	i. d.	1.06	2.70	1.06	2.70
	thickness	0.12	0.32	0.12	0.32

(2) The i. d. diameter of the gasket recess should be the same as that of the gasket but the o. d. diameter should be somewhat greater than the o. d. diameter of the gasket in order to permit the expansion of the latter.

The bomb assembly consists of: a chamber, bomb head and bomb head cover, fabricated out of a roll (15 × 3 inches for bomb B) of annealed chrome vanadium steel, S. A. E. 6140, from the Crucible Steel Company, 17 East 42d Street, New York City; a copper gasket; a thrust plate; six $^{7}/_{16} \times 1^{1}/_{4}$ inch socket head cap screws of high tensile steel with 20 threads to the inch supplied by the Allen Manufacturing Company, Hartford, Connecticut; a 7.5 cm. length of 3 mm. copper tubing, for inlet of hydrogen, screwed into the hydrogen inlet on the lower face of the bomb head. A wrench to fit the standard coupling on the steel tubing and one to fit the cap screws and a small vise are necessary for opening and closing the bomb. The chamber should be protected from the pipe jaws of the vise by pieces of sheet copper.[3]

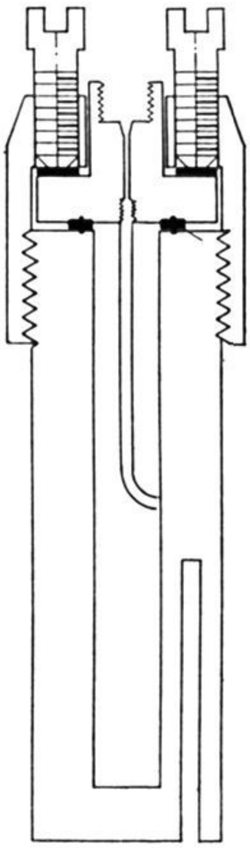

Fig. 1.—Cross section of bomb.

The procedure for standardizing the bomb is as follows. A standard solution of acetone or acetoacetic ester is made up of such a strength that 0.25 mole of the keto compound is contained in 100 ml. of an ethanol solution. Twenty ml. of the solution is placed in the chamber with 1 g. of copper–chromium oxide catalyst. The chamber is placed upright in the vise, the copper gasket placed in the gasket recess in the head, and the head put in position. The thrust plate is placed on the bomb head, and the bomb head cover screwed down to within a quarter of a turn as far as it will go. The cap screws are then turned down. The nipple (attached to the valve) is screwed into the bomb head. Care should be taken that the gage and the open end of the bent copper tube are so placed that both are pointing upward when the bomb assembly is later placed in the shaker. The bomb is then removed from the vise, and the valve connected to a hydrogen tank by the opening in the valve opposite the gage. Hydrogen is allowed to enter to the desired pressure. The valves on the tank and the bomb are closed and the bomb assembly detached from the connection to the tank. The bomb is then placed in the heater, mounted on a shaker, and the thermocouple put in place. After a few minutes of agitation of the contents of the bomb the pressure indicated on the gage will become constant if the connections are all tight. The procedure from this point on is essentially the same as that previously described.[1]

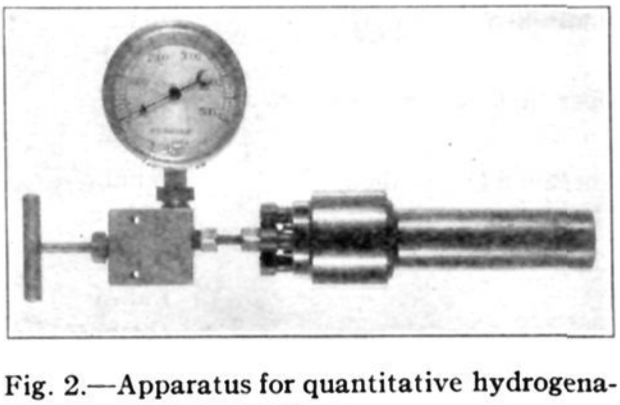

Fig. 2.—Apparatus for quantitative hydrogenation.

The temperature to be used is a function of the compound involved—150° for the hydrogenation of a ketone, and 250° for a carbethoxy group, for example. The heater for bomb (A) should contain about 30 feet of No. 22 nichrome wire in order to carry a current of about 3.7 amperes on 110 volts, while the heater for bomb (B) should have two coils connected in parallel, each 40 feet

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(3) The bombs described herewith were constructed by Mr. Lee Henke of this Laboratory.

in length. After reaction is complete the bomb may be removed immediately from the heater and allowed to cool to room temperature.

A number of compounds that are quantitatively hydrogenated may be used for purposes of standardization. The amount of compound used should be such as to bring about a drop in hydrogen pressure of 300 to 800 pounds. Ethanol or methylcyclohexane are suitable solvents for temperatures below 200°. Above that temperature butanol is more satisfactory in quantitative work, since its vapor pressure and coefficient of expansion are smaller. Nickel as well as copper-chromium oxide has been used as a catalyst.[4]

As a result of several determinations a pressure drop of 750 ± 10 pounds in bomb (A) was found to correspond to the hydrogenation of 0.05 mole of acetone or acetoacetic ester made up to 20 ml. This amount corresponds to a drop in pressure of 15,000 pounds per mole of hydrogen absorbed. The drop in pressure per mole of hydrogen is a function of the volume of hydrogen in the bomb so that with 10 instead of 20 ml. of liquid in the bomb, the drop in pressure per mole of hydrogen was found to be 10,500 to 10,800 (av. 10,700) pounds per mole in six determinations with acetone, acetoacetic ester, ethyl laurate and diethyl sebacate. The drop in pressure was 2800 pounds per mole of hydrogen for bomb B containing 50 ml. of liquid. The figures given are based upon pressure readings made while the temperature of the gas was approximately 23°.

In order to control the extent of hydrogenation it is important to be able to convert the pressure reading at the temperature of hydrogenation to the pressure reading at 23°. For this purpose the following figures, when used as divisors, have been found to give approximately the pressures at 23° in bomb A: 1.22 for 100°, 1.31 for 130°, 1.40 for 160°, 1.52 for 200° and 1.67 for 250°. These figures are less than would be calculated from the gas laws primarily because a portion of the hydrogen is in the Bourdon tube of the gage and consequently is not heated much above room temperature. They are not true for ethanol as a solvent at temperatures above 200°. The corresponding figures for bomb B may be calculated sufficiently accurately from the gas laws.

The tightness of the apparatus is indicated by the fact that bomb A containing hydrogen under a pressure of 100 atmospheres at 23° with butanol and copper-chromium oxide catalyst has been heated to 250° (167 atmospheres) and cooled to room temperature on five successive days without opening. At the end of the period the pressure registered by the gage was within 1 atmosphere of that originally observed. Thus the leakage, if any, of hydrogen from the bomb was less than 20 ml. of gas. The same gasket has been used almost daily for several weeks at 150 to 250° without a detectable leakage. The apparatus and procedures given above have been found repeatedly to give results which were reproducible within from 0.001 to 0.003 mole of hydrogen. Duplicate analyses made by Mr. Leo Kuick for ethyl nicotinate in a mixture with ethyl nipecotate over nickel at 165° showed 23.0 and 24.2% of the nicotinate for example.

Summary

Procedures and apparatus have been described which are useful for quantitative catalytic hydrogenations under pressures of 100 to 300 atmospheres.

MADISON, WISCONSIN

RECEIVED JUNE 19, 1933
PUBLISHED OCTOBER 6, 1933

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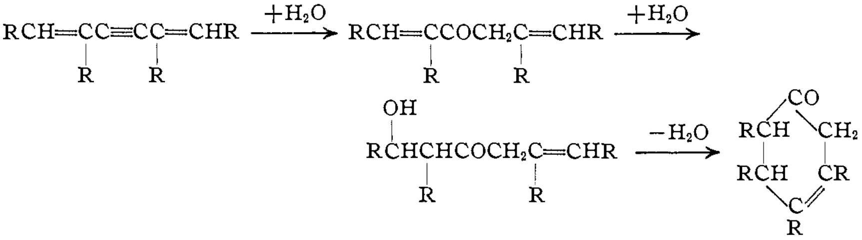
[4] If the bomb has not been used for several days, a film of oxide may form on the inside of the chamber so that it is advisable to make one or two preliminary hydrogenations at 250° before attempting quantitative work.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Cyclization of Substituted Divinylacetylenes

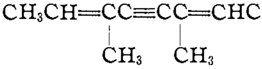
BY D. T. MITCHELL AND C. S. MARVEL

An investigation of the reactions of some substituted divinylacetylenes showed that treatment with sulfuric and acetic acids caused these dienines to undergo an unexpected hydration and cylization.[1] The following mechanism was proposed for the reaction:



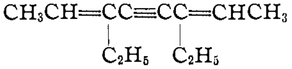
The oxidation and reduction products of the unsaturated ketone obtained from 4,7-di-*n*-propyldecadiene-3,7-ine-5 supported the cyclic structure which was assigned to it.

The unusual ring closure has now been observed in the case of two other tetrasubstituted divinylacetylenes, 3,6-dimethyloctadiene-2,6-ine-4 (I) and 3,6-diethyloctadiene-2,6-ine-4 (II). The cyclization of the tetramethyl derivative (I) could be accomplished only at low temperatures (0°). At room temperature only tarry polymerization products were produced. The dimethyldiethyl derivative (II) gave a good yield of cyclic ketone when the reaction was carried out at room temperature. No conditions were discovered which would enable us to apply this cyclization reaction to 2,5-dimethylhexadiene-1,5-ine-3 (III), although a wide range of temperature and acid concentration was tried. It is apparent that this cyclization reaction cannot be applied in a satisfactory manner to the disubstituted dienines where polymerization takes place rapidly.



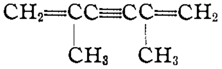
$CH_3CH{=}\underset{CH_3}{C}C{\equiv}C\underset{CH_3}{C}{=}CHCH_3$

I



$CH_3CH{=}\underset{C_2H_5}{C}C{\equiv}C\underset{C_2H_5}{C}{=}CHCH_3$

II



$CH_2{=}\underset{CH_3}{C}C{\equiv}C\underset{CH_3}{C}{=}CH_2$

III

The mechanism which was previously proposed for the cyclization has been established by further experiments using 3,6-dimethyloctadiene-2,-6-ine-4 (I). The unsaturated ketone formed by the cyclization reaction has been shown to be 2,3,4,5-tetramethylcyclohexen-4-one-1 (IV) by ozonization which gave the known α,β-dimethyl-γ-ketovaleric acid (V) and by dehydrogenation to 2,3,4,5-tetramethylphenol (VI). Furthermore, the ketone was reduced to a hexahydroprehnitene (VII) which by dehydrogenation gave prehnitene (VIII).

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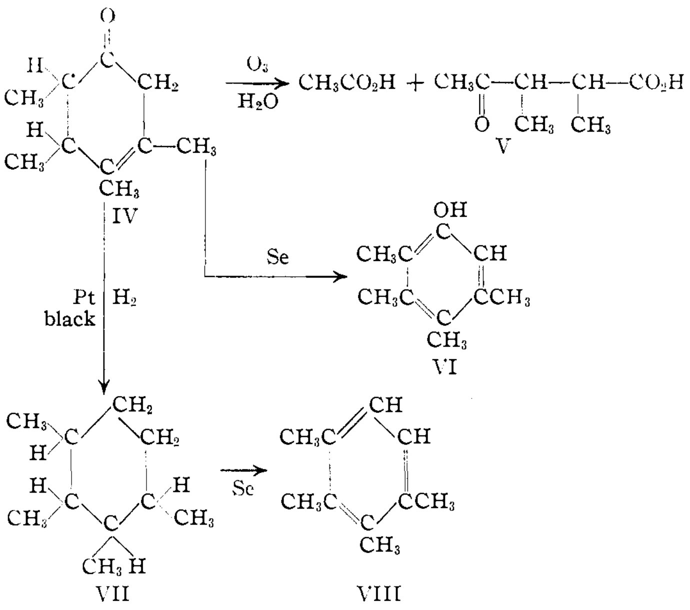
[1] Blomquist and Marvel, THIS JOURNAL, **55**, 1655 (1933).



Experimental

Preparation of the Divinylacetylenes.—Tetramethylbutinediol, *sym*-dimethyldiethylbutinediol and tetraethylbutinediol were obtained in 70–90% yields as described by Dupont.[2] The dehydration of tetramethylbutinediol with sulfuric acid according to Dupont's[2] procedure was unsatisfactory. The best yields of 2,5-dimethylhexadiene-1,5-ine-3 were obtained by dehydrating the glycol with 60% phosphoric acid in an atmosphere of carbon dioxide. A solution of 25 g. of the glycol in 250 cc. of 60% phosphoric acid in a 500-cc. three-necked flask was distilled slowly. A fairly rapid current of carbon dioxide was passed through the boiling mixture and water was added from a dropping funnel to keep the concentration of the acid at about 60%. In about one-half hour the reaction was complete. The hydrocarbon was separated from the distillate, dried over magnesium sulfate and distilled under reduced pressure. The yield was 11–12 g. (60–70%) of a product boiling at 35° (5 mm.). Distillation at atmospheric pressure caused most of the hydrocarbon to polymerize.

The tetrasubstituted divinylacetylenes, 3,6-dimethyloctadiene-2,6-ine-4 and 3,6-diethyloctadiene-2,6-ine-4 were readily obtained in 75–85% yields by Dupont's procedure.[2] These hydrocarbons were more stable and did not polymerize so readily. The diethyl derivative has not been reported previously. It has the following properties: b. p. 80–81° (5 mm.); n^{20}_{D} 1.4965; d^{20}_{4} 0.8196.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.80; H, 11.19. Found: C, 89.00; H, 11.30.

This hydrocarbon was ozonized in carbon tetrachloride and the ozonide was decomposed with water. The α-ketobutyric acid was identified as the phenylhydrazone of m. p. 150°[3] and acetic acid was identified as the *p*-bromophenacyl ester, m. p. 84–85°.[4]

Preparation and Characterization of the Substituted Cyclohexenones.—The dienines were converted to the cyclic unsaturated ketones by the general procedure de-

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(2) Dupont, *Ann. chim.*, [8] **30**, 485 (1913).

(3) Barre, *Compt. rend.*, **184**, 825 (1927), gives this melting point at 152° on slow heating.

(4) Judefind and Reid, THIS JOURNAL, **42**, 1043 (1920), give the melting point as 84–85°.

scribed in the previous paper.[1] Several variations of the experimental details were tried in the case of 2,5-dimethylhexadiene-1,5-ine-3 but only tarry products could be obtained. The cyclization of 3,6-dimethyloctadiene-2,6-ine-4 had to be carried out at 0° since at room temperature only tarry products were formed. The diethyl derivative reacted well at room temperature. The unsaturated ketones were characterized by preparing the 2,4-dinitrophenylhydrazones and by reduction to the saturated hydrocarbons by methods previously described in detail.[1] The new derivatives and their properties are given in Table I.

TABLE I

PROPERTIES OF SOME NEW CYCLOHEXANE DERIVATIVES

	Compound	Yield, %	B. p., °C. (mm.)	M. p., °C.
1	2,3,4,5-Tetramethylcyclohexene-4-one-1	25	84–86 (5)	.....
2	2,4-Dinitrophenylhydrazone	..	.....	158–159
3	1,2,3,4-Tetramethylcyclohexane	85	84 (5)	.....
4	3,4-Dimethyl-2,5-diethylcyclohexene-4-one-1	36	104–107 (5)	.....
5	2,4-Dinitrophenylhydrazone	..	.....	138–139
6	1,2-Dimethyl-3,6-diethylcyclohexane	75	91–92 (4)	.....

				Analyses, %			
				Carbon		Hydrogen	
	n_D^{20}	d_4^{20}	Formula	Calcd.	Found	Calcd.	Found
1	1.4690	0.9298	$C_{10}H_{16}O$	78.87	78.90	10.60	10.75
2	....	....	$C_{16}H_{20}N_4O_4$	N, 16.86; found, 17.03			
3	1.4531	.8219	$C_{10}H_{20}$	85.62	85.73	14.38	14.54
4	1.4820	.9152	$C_{12}H_{22}O$	79.93	79.82	11.19	11.15
5	....	....	$C_{18}H_{24}N_4O_4$	N, 15.50; found, 15.69			
6	1.4673	.8536	$C_{12}H_{24}$	85.62	85.70	14.38	14.47

Ozonization of 2,3,4,5-Tetramethylcyclohexene-4-one-1.—This ozonization and the subsequent hydrolysis were carried out by the procedures described before.[1] The acid volatile with steam was identified as acetic acid by converting it to the *p*-bromophenacyl ester, m. p. 84–85°.[4] The non-volatile acid boiled at 120° (5 mm.) and was identified as α,β-dimethyl-γ-ketovaleric acid.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.29; H, 8.33; neutral equivalent, 144.1. Found: C, 58.41; H, 8.42; neutral equivalent, 142.0.

The *p*-nitrophenylhydrazone was prepared and found to melt at 123°. This derivative has previously been recorded as melting at 121–123°.[5]

Dehydrogenation of 1,2,3,4-Tetramethylcyclohexane.—Two grams of this hydrocarbon was dropped onto powdered selenium previously heated to about 400°. The distillate was condensed and combined with an ether extract of the cooled selenium. The extract was washed with water, dried over magnesium sulfate, filtered and distilled. A fraction was collected from 190–210° and then carefully refractionated. The product weighed 0.75 g., b. p. 202–203° (745 mm.); n_D^{20} 1.5211; d_4^{20} 0.9017. A sample of prehnitene[6] had the following constants; b. p. 203° (760 mm.); n_D^{20} 1.5203; d_4^{20} 0.9010.

Dehydrogenation of 2,3,4,5-Tetramethylcyclohexene-4-one-1.—Ten grams of this ketone was dehydrogenated by the procedure described for the hydrocarbon. The ether solution of the crude distillate was extracted with 5% sodium hydroxide solution. The alkaline solution was separated and acidified. The phenol which separated was

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(5) Willstätter and Brossa, *Ber.*, **44**, 2192 (1911).

(6) We are greatly indebted to Professor Lee Irvin Smith for the prehnitene which was used for this experiment and for the preparation of 2,3,4,5-tetramethylphenol.

collected in ether, the ether was evaporated and the residue was recrystallized from benzene. About 0.1 g. of a product of m. p. 80° was obtained. The melting point of this product was not depressed by mixing it with a sample of 2,3,4,5-tetramethylphenol prepared from prehnitene.[7] Limpach gives the melting point of this phenol as 80–81°.[8]

Summary

1. The cyclization of substituted divinylacetylenes has been extended to 3,6-dimethyloctadiene-2,6-ine-4 and 3,6-diethyloctadiene-2,6-ine-4. The reaction could not be applied to the disubstituted divinylacetylene, 2,5-dimethylhexadiene-1,5-ine-3.

2. The structure proposed for the ring compounds and the mechanism of the cyclization reaction have been established by converting the cyclohexane derivatives obtained from 3,6-dimethyloctadiene-2,6-ine-4 to known derivatives of tetramethylbenzene.

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(7) Cummings, Hopper and Wheeler, "Systematic Organic Chemistry," Constable and Co., London, 1931, pp. 323, 210.

(8) Limpach, *Ber.*, **21**, 645 (1888).

URBANA, ILLINOIS

RECEIVED JUNE 19, 1933
PUBLISHED OCTOBER 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Dehalogenation of Aliphatic Bromo Acids. The Bromo and Dibromo Olefins*

BY G. BRYANT BACHMAN

Dehalogenation of cinnamic acid dibromide may lead to the formation of cinnamic acid, α-bromocinnamic acid, α-bromoallocinnamic acid or ω-bromostyrene or mixtures of all of these depending upon the conditions of dehalogenation and particularly on the nature of the dehalogenating base used. In the aliphatic series the dehalogenation of α,β-dibromo acids has been less thoroughly studied and although the bromoolefins analogous to ω-bromostyrene have been detected among the products in some cases, attention has generally been centered on the relative yields of α-bromo and α-bromoisoolefinic acids. No systematic efforts have been made to isolate the 1-bromo-1-olefins formed and determine their physical and chemical properties and their yields.

There are apparently two other well-defined methods available for the preparation of 1-bromo-1-olefins (1) the dehalogenation of olefin di-dibromides

$$2RCHBrCH_2Br + \text{Alc. KOH} \longrightarrow \begin{matrix} RCH{=}CHBr \\ +RCBr{=}CH_2 \end{matrix} + 2KBr + 2H_2O \qquad (1)$$

and (2) a method recently devised by Kirrmann.[1] Neither of these meth-

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* Presented before the Organic Section at the Chicago Meeting of the American Chemical Society, September, 1933.

(1) Kirrmann, *Bull. soc. chim.*, **41**, 316–323 (1926).