Table IV

Ketoximes

Oxime of	$n^{25}D$	B. p. °C.	Mm.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
5-Ethyl-3-heptanone	1.4547	75–79	1	68.79	12.10	68.48	12.26
3-Decanone	1.4532	81	1	70.18	12.28	69.94	12.46
5-Ethyl-3-nonanone	1.4560	89–92	1	71.35	12.43	71.05	12.47
4-Ethyl-2-hexanone	1.4522	69	1	67.18	11.89	67.13	12.06
5-Methyl-3-hexanone	1.4428	55	1	65.12	11.63	65.32	11.89
3-Heptanone[a]	1.4522	56	1	65.12	11.63	65.45	11.87
3-Nonanone	1.4552	70	1	68.79	12.10	69.14	12.38
4-Ethyl-2-octanone	1.4534	81	1	70.18	12.28	70.31	12.41

[a] Timmermans, *Bull. soc. chim. Belg.*, **36**, 502 (1927).

extracted with ether in a Soxhlet extractor to recover absorbed oxime. The ether extract was added to the filtrate and the ether removed on a water-bath. The acetic acid was removed in a low vacuum and the residue, a greenish oil, distilled at 89–92° (1 mm.); yield 21 g. (52%). The yields of oxime were consistently 50–60%. They are viscous, strong-smelling liquids. Their properties are given in Table IV.

Preparation of Ketones: 5-Ethyl-3-nonanone.—The above oxime (17.5 g.) was refluxed one-half hour with 50 cc. of 4 *N* sulfuric acid and 22 cc. of formalin solution. The ketone was extracted with two 50-cc. portions of ether and the ether solution dried over anhydrous copper sulfate or Drierite. The ether was removed on a water-bath and the ketone distilled; b. p. 53° (1 mm.); yield 12 g. (80%).

Anal. Calcd. for $C_{11}H_{22}O$: C, 76.92; H, 12.82. Found: C, 76.62; H, 12.97.

This ketone, not described in the literature, was the only one of the ketones which would not form a solid derivative. The melting points of the semicarbazones of the other ketones agreed with those reported in the literature.

The reduction of 35 g. of 2-nitro-4-ethyl-3-hexene with hydrogen and Raney nickel at 45 lb. yielded 10 g. of 4-ethyl-2-hexanone as the principal product. A large amount of tar remained in the distilling flask.

Summary

A variety of aliphatic nitroölefins have been prepared in good yield by refluxing the acetates of nitroalcohols with an aqueous methanol solution of sodium bicarbonate.

Nitroölefins of suitable structure were reduced to the corresponding ketoximes in 50–60% yield by means of zinc and acetic acid.

The ketoximes were converted to ketones by hydrolysis with dilute sulfuric acid in the presence of formalin.

The α-naphthyl urethans of a number of nitroalcohols have been described.

Columbia, Missouri Received September 18, 1943

[Contribution from the Department of Chemistry, University of California at Los Angeles]

The Reaction of Citronellal with Benzylmagnesium Chloride[1]

By William G. Young and Samuel Siegel

In attempting to prepare α-benzylcitronellol by the addition of citronellal to benzylmagnesium chloride, Rupe[1a] isolated an almost colorless, viscous liquid, distilling at 243–244°(9 mm.). After determining the elementary analysis for carbon and hydrogen, and the value of the molecular weight of the substance in benzene, he suggested that this material was formed by the addition of two moles of benzylmagnesium chloride to one mole of citronellal, the second mole of the Grignard reagent adding to the ethylenic double bond of the aldehyde. Later Gilman and Schulz[2] sought to disprove this contention by an indirect method. They added the aldehyde to a large excess of benzylmagnesium chloride. The mixture was then treated with carbon dioxide and the resulting acids were isolated. Since the product of the addition of a Grignard reagent to an ethylenic double bond would contain a carbon to magnesium linkage, it should react with carbon dioxide to form the salt of a carboxylic acid. Gilman and Schulz isolated phenylacetic acid but found no indication of the presence of any other acid. They concluded that the Grignard reagent had not added to the ethylenic double bond. Although these workers also isolated a liquid having the same properties as that reported by Rupe, they did not further investigate it. Since this indirect proof is not conclusive[3,4] and because certain evidence obtained in this Laboratory pointed to the possibility of the addition of Grignard reagents to the ethylenic double bond, a more thorough investigation of the above reaction was carried out.

Although Rupe was unable to obtain better than a 25% yield of α-benzylcitronellol, we have

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[1] Presented before the Division of Organic Chemistry at the Pittsburgh meeting of the American Chemical Society, Sept., 1943.

[1a] Rupe, *Ann.*, **402**, 161 (1913).

[2] H. Gilman and W. F. Schulz, This Journal, **52**, 3588–3590 (1930).

[3] Kharasch, *Ann. Survey of Am. Chem.*, **5**, 193 (1930).

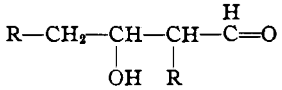
[4] Gilman and Schulz, This Journal, **53**, 2799–2801 (1931).

been able to increase the yield to 80% by using an excess of the Grignard reagent. An excess of aldehyde gives 70–80% of the more complex product.

The complex material (which will hereafter be designated substance A) appeared to be homogeneous after several distillations. The elementary analysis and molecular weight indicated the formula $C_{27}H_{44}O_2$ (molecular weight, 400). There are two ethylenic double bonds and two active hydrogen atoms per molecule. Quantitative acetylation with acetic anhydride leads to the same value for the number of hydroxyl groups per molecule. There are also two citronellyl radicals per molecule. This was determined by comparing the amount of acetic acid obtained from A upon oxidation with chromic acid with that obtained upon identical treatment of α-benzylcitronellol.[5] Oxidation of A with alkaline potassium permanganate led to the formation of phthalic acid, which was recovered in good yields. No benzoic acid was isolated.

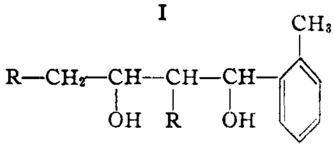
When A was heated with potassium acid sulfate, one molecule of water was lost. The resulting substance (B) contained one oxygen atom per molecule but neither an active hydrogen atom nor a carbonyl group. It was therefore a cyclic ether (IV).

It is conceivable that A could have been formed in one of the following ways. (1) Two molecules of the aldehyde, under the influence of the Grignard reagent, might condense to form an aldol (I). This aldol would then react with a molecule of benzylmagnesium chloride at the ortho position (to satisfy the condition that phthalic acid be obtained after oxidation) to give, after hydrolysis, the glycol (II).

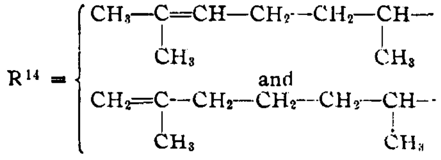


$$\mathrm{R-CH_2-\underset{OH}{CH}-\underset{R}{CH}-\overset{H}{C}=O}$$

I

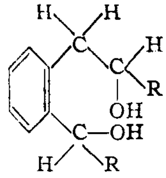


II

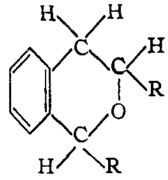


$$R^{14} = \begin{cases} \mathrm{CH_3-\underset{CH_3}{C}=CH-CH_2-CH_2-\underset{CH_3}{CH}-} \\ \text{and} \\ \mathrm{CH_2=\underset{CH_3}{C}-CH_2-CH_2-CH_2-\underset{CH_3}{CH}-} \end{cases}$$

(2) Two molecules of the aldehyde and one molecule of benzylmagnesium chloride might react in such a way that one molecule of the aldehyde would become attached to the ortho position, the other to the methylene group of the benzyl radical as in III.



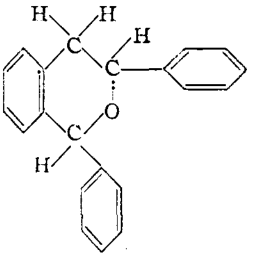
III



IV

The first path for the formation of A was disproved when it was shown that the product isolated from the reaction of the aldol of citronellal with benzylmagnesium chloride was the "normal" addition product (*i. e.*, it was oxidized to benzoic acid and not phthalic acid) and furthermore it readily lost two molecules of water to form a hydrocarbon.

The second path is in complete agreement with all observations. The glycol III should be dehydrated easily to form the cyclic ether IV. Indeed Schmidlin and Garcia-Banûs[6] have shown that benzaldehyde reacts with benzylmagnesium chloride to form a compound, analogous to III, which dehydrated during distillation and formed diphenylisochromane V.



V

The above results prove the correctness of the statement of Gilman and Schultz that benzylmagnesium chloride does not add to the ethylenic double bond of citronellal.

Discussion

In the reaction of benzylmagnesium chloride with citronellal, the concentration and order of addition of reactants play an important role in determining the character of the reaction products. If a large excess of Grignard reagent is used, a good yield of α-benzylcitronellol is obtained. In the formation of this compound, one mole of Grignard reagent and one mole of aldehyde have combined and no abnormal reaction has occurred. On the other hand, if equal amounts of the aldehyde and benzylmagnesium chloride are used, the product is largely one in which two moles of aldehyde and one mole of Grignard reagent have united. In this case the Grignard reagent has reacted abnormally since phthalic acid is obtained upon oxidation of the product.

Johnson[7] has suggested that "the normal and abnormal reactions are to be regarded as two possible transpositions within the initial coördination

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(5) Karrer, Helfenstein, Wehrli and Wellstein, *Helv. Chim. Acta*, **13**, 1084–1098 (1930).

(6) Schmidlin and Garcia-Banûs, *Ber.*, **45**, 3193 (1912).

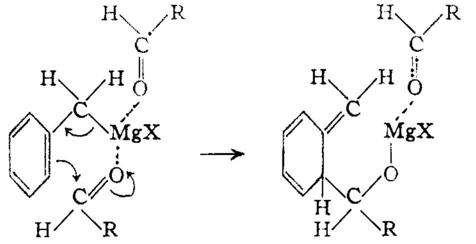
(7) Gilman, "Organic Chemistry," second ed., John Wiley and Sons, Inc., New York, N. Y., 1943, Chap. XXV, p. 1880.

complex which is formed as the first step in all Grignard reactions." This mechanism does not explain how a change in the relative concentrations of reactants can influence the ratio of normal to abnormal products.

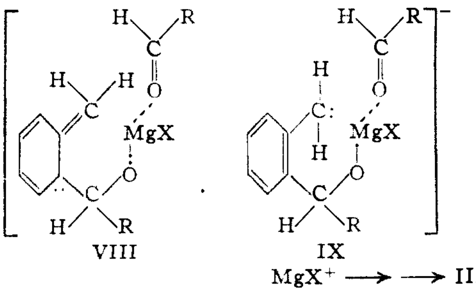
Though the intimate mechanism for the normal reaction may be as described by Johnson, the mechanism for the abnormal reaction must be modified.

The relationship of concentration of reactants to the kind of product formed suggests that different intermediates are required for the normal and abnormal reaction paths. Since the abnormal reaction is favored by high concentrations of aldehyde, it is reasonable to suppose that the reaction complex for the abnormal reaction contains a larger number of aldehyde molecules than in the case for the normal reaction. Each complex may then react in a manner peculiar to itself and give rise to different products.

The coördination of several aldehyde molecules with one molecule of Grignard reagent may increase the tendency toward ionization of the carbon to magnesium bond and thus permit the activation of the ortho position through resonance (VI). Since the aldehyde molecules within the complex would be polarized and also situated favorably for further reaction, they would be expected to form most easily a bond at the ortho position. The resulting complex (VII) has an active hydrogen atom at the substituted ortho position, since by its removal, the benzenoid system is restored. This proton could be removed readily by another molecule of the Grignard reagent forming toluene and the intermediate VIII. In turn, this intermediate would be expected to react at the methylene position with a second molecule of the aldehyde since the resonance structure IX would contribute more to the stability of the ion than the non-benzenoid structure with the electron pair at the ortho or para position.



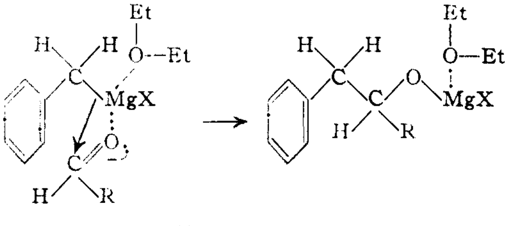
VI VII



VIII IX

MgX⁺ ⟶ ⟶ III ⟶ IV

The coördination of only one aldehyde molecule with the Grignard reagent apparently does not allow for activation of the ortho position but leads to a normal reaction as follows



Experimental

Benzylmagnesium chloride was prepared in excellent yields (99%) by adding a solution of freshly distilled benzyl chloride (0.663 mole) in ether (200 ml.) to an excess of magnesium turnings (0.830 mole) covered with ether (100 ml). The Grignard reagent was filtered through glass wool before it was used.

To this vigorously stirred solution, cooled in an ice-bath, freshly distilled citronellal (52.0 g., 0.338 mole) was added dropwise. After the aldehyde had been added, the reaction mixture was allowed to warm up to room temperature (about two hours). It was hydrolyzed by pouring it over a mixture of cracked ice and ammonium chloride. The heat of the reaction melted the ice, leaving two phases These were separated. The aqueous phase was extracted again with ether (100 ml.). The ether extracts were combined, washed with a little water, and dried over potassium carbonate. After the solvent was removed, the ethereal concentrate was transferred to a 250-ml. Claisen flask and distilled at reduced pressure.

Four fractions were obtained: (1) 27.0 g., distilling below 30°(4 mm.) (trapped in dry-ice); (2)12.0 g., b. p. (4 mm.) 75-100°; (3) 40.5 g., b. p. (3 mm.) 153-175°; (4) 21.5 g., b. p. (3 mm.) 200-235°. The boiler residue showed little or no decomposition.

When redistilled at atmospheric pressure, fraction (1) yielded 20 g. of toluene (b. p. 100-110°), the forerun being ether.

Fraction (2) was distilled at reduced pressure and arbitrarily separated into four fractions: (a) 1.1 g., b. p. (3 mm.) 60-62.5°, $n^{24.5}\mathrm{D}$ 1.4622; (b) 4.8 g., b. p. (3 mm.) 62.5-65°, $n^{24.5}\mathrm{D}$ 1.4762; (c) 1.6 g., b. p. (3 mm.) 65-70°. $n^{24.5}\mathrm{D}$ 1.4948; (d) 1.4 g., b. p. (3 mm.) 75-116° $n^{24.5}\mathrm{D}$ 1.4878. The first two fractions chiefly consist of isopulegol (b. p. (12 mm.) 91°, $n^{17}\mathrm{D}$ 1.4729) contaminated by some benzyl alcohol (b. p. (10 mm.) 93°, $n^{20}\mathrm{D}$ 1.5396). The last two fractions contain more benzyl alcohol. The isopulegol was identified through the preparation of its allophanate, m. p. 218-219°.[8] Benzyl alcohol was identified through the preparation of the acid phthalate, m. p. 103-105°; *p*-nitrobenzoate, m. p. 77-79°; and the 3,5-dinitrobenzoate, m. p. 110-111°.

Fraction (3) was α-benzylcitronellol, b. p. (3 mm.) 153-156°, $n^{24.5}\mathrm{D}$ 1.5079. Oxidation of this material (2.01 g.) with alkaline potassium permanganate produced benzoic acid (0.815 g.) and approximately 3 mg. of a chloroform insoluble acid m. p. 170-185° which on sublimation gave phthalic anhydride, m. p. 130°.

When fraction (4) was redistilled, the main portion had the properties: b. p. (3 mm.) 234-235°, $n^{24.5}\mathrm{D}$ 1.5120. According to the experimental procedure this fraction should correspond to the substance, which was claimed by Rupe to be the product formed by the addition of a molecule of the Grignard reagent to the ethylenic double bond in citronellal. However, it will be shown later that his material was apparently a dehydration product of the one we isolated.

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(8) Béhal, *Bull. soc. chim.*, [4] **25**, 477 (1919).

The material, substance A, contained only carbon, hydrogen, and oxygen. It appeared to be homogeneous.

Anal. Calcd. for $C_{27}H_{44}O_2$: C, 80.93; H, 11.08. Found: C, 80.82; H, 11.07.

Identification of Substance A.—The molecular weight was determined cryoscopically in camphor[9] and also in benzene. In the first solvent the values were 360–370 and in the second 484–490 compared with the calculated value, 400. The high value for the molecular weight in benzene indicates association of the solute in that solvent. This phenomenon indicates that Rupe had isolated substance B, an ether, rather than substance A, a glycol. The analysis, he reported (C, 85.10; H, 10.28), is also in fair agreement with the values calculated for the cyclic ether (B) (see below).

Because of the difficulty of identifying the substance by simple degradations, a number of quantitative and semi-quantitative measurements for the various structural units in the substance were carried out.

The number of double bonds per molecule was estimated by means of quantitative bromination[10] and by hydrogenation with a barium sulfate-supported palladium catalyst.[11] The first method indicated 2.04 double bonds, the second 1.84 double bonds per molecule.

The Zerewitinoff method for estimating active hydrogen[12] showed 1.9–2.2 active hydrogens per molecule. No carbonyl groups were present.

A quantitative acetylation showed 1.90 hydroxyl groups per molecule.[13]

The number of citronellyl radicals in the molecule was determined by finding the amount of acetic acid which could be obtained by oxidation of the substance with chromic acid.[5] Since citronellal consists of a mixture of the isomeric limonene and terpinolene forms,[14] it was necessary to compare the amount obtainable from a compound prepared from the same sample of aldehyde. α-Benzylcitronellol, which was formed in the same reaction mixture as A, was used for this purpose.

Karrer's procedure[5] was modified, in order to separate the acetic from the benzoic acid, by following the suggestions of Young, Ballou and Nozaki.[15] In this way, α-benzylcitronellol forms 1.14–1.16 moles of acetic acid per mole of compound while A forms 2.61–2.66 moles of acetic acid per mole of A. This is in fair agreement with the presence of two citronellyl radicals per molecule of A.

Pyridine proved to be far superior to water as a solvent for the oxidation of A with potassium permanganate.[16] In this solvent, 1.09 g. of A yielded 0.325 g. of crude phthalic acid. This was identified by its melting point and the melting point and mixed melting point of the anhydride. No benzoic acid was isolated. This shows that substance A is the "abnormal" reaction product of benzylmagnesium chloride.

Dehydration of A.—Four grams of A was placed in a 10-ml. distilling flask. Potassium acid sulfate (1.0 g.) was added. The mixture was heated to 160° under reduced pressure (thirty minutes) until no more water was evolved. Another gram of the acid salt was then added and the heating continued. After one hour of this treatment, the contents of the flask were cooled and the oil which remained was separated from the acid with the aid of a little ether. This ethereal solution was washed with water and dried with magnesium sulfate. The product was then distilled at reduced pressure. A faintly yellow oil was obtained, b. p. (3 mm.) 215–217°, $n^{25.5}\text{D}$ 1.5090.

Anal. Calcd. for $C_{27}H_{42}O$; C, 84.77; H, 11.07. Found: C, 85.12; H. 10.83.

The analysis above shows the presence of one oxygen atom per molecule. This was shown to be neither a part of a hydroxyl group nor a carbonyl group by the Zerewitinoff method.[17] Bromination led to the value of 182 g. per double bond. Therefore, the dehydration product (B) must be a cyclic ether.

Preparation of the Aldol of Citronellal.—Citronellal (50 g., $n^{23}\text{D}$ 1.4479) was added slowly to a solution of potassium hydroxide (2 g.) in 50 ml. of 95% ethanol. The mixture was cooled in ice during the addition. A single phase resulted. The reaction mixture was allowed to stand overnight in a refrigerator. In the morning the solution had become slightly yellow. It was shaken at intervals and kept cold for eleven hours longer. The solution was poured into 200 ml. of water and 50 ml. of ether was added to aid in the separation of the reaction product. This ether phase was washed with sodium bicarbonate solution, then with water and finally dried over sodium sulfate. After the solvent was removed, the product was distilled rapidly under reduced pressure. A colorless liquid (b. p. (5 mm.) 170.5–173.0°; $n^{21.5}\text{D}$ 1.4850) was obtained (34 g. or 64% yield). Nine grams of lower boiling material (unreacted aldehyde) also was obtained. The aldol appeared to have become dehydrated to the extent of about 10%. This is indicated by the unsaturation to bromine. Calcd.: 165 g. per double bond; found, 142 g. per double bond.

To check upon the amount of Canizzaro reaction taking place, the aqueous phase from the preparation was acidified and extracted with ether. A small amount of a colorless oil was obtained (less than 1 g.).

Reaction of the Aldol with Benzylmagnesium Chloride.—A solution of 0.241 mole of benzylmagnesium chloride in 180 ml. of ether was cooled in an ice-bath. The aldol (25.0 g., 0.0815 mole) dissolved in 30 ml. of ether was added dropwise to the vigorously stirred Grignard reagent. After the addition of the aldol was completed, the mixture was allowed to warm up to room temperature. The product was hydrolyzed with cracked ice and ammonium chloride. The ether phase was separated, washed with water, and dried with anhydrous sodium sulfate. After the solvent was removed, the product was distilled rapidly from a Claisen flask at reduced pressure. The product (23.8 g.) was collected over a 10° range, b. p. (4 mm.) 226–236°; $n^{28.5}\text{D}$ 1.5157; unsaturation to bromine: calcd., 200 g. per double bond; found, 148 g. per double bond. The product was more fluid than substance A. This is probably due to the partial dehydration of the former.

Oxidation of the Product of the Grignard Reaction with the Aldol.—The product (1.42 g.) of the above Grignard reaction was oxidized by potassium permanganate in pyridine under conditions identical with those employed for substance A. There was isolated, in purified form, 0.256 g. of benzoic acid and six milligrams of phthalic acid. The latter was characterized by the melting point of the anhydride and by the brilliant fluorescein test.[18]

Dehydration of the Product of the Grignard Reaction with the Aldol.—The product (17.0 g.) of the reaction of the Grignard reagent with the aldol was dehydrated under conditions identical with those described previously for the dehydration of substance A. The crude distillate was collected over a twelve degree range, 203–215° (3 mm.). The middle fraction was redistilled and used for the analysis reported. Properties: b. p. (3 mm.) 204–206°, $n^{24.5}\text{D}$ 1.5278.

Anal. Calcd. for $C_{27}H_{40}$; C, 88.95; H, 11.06. Found: C, 88.81; H, 11.10; unsaturation to bromine, 134 g. per double bond.

The dehydration product is therefore a hydrocarbon. The value for the amount of unsaturation indicates that the product had partially cyclized during the treatment with acid. This was not unexpected.[14] If the material had not cyclized the weight per double bond would have been 91 g.

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[9] Smith and Young, *J. Biol. Chem.*, **75**, 289 (1927).

[10] A. W. Francis, *Ind. Eng. Chem.*, **18**, 821 (1926).

[11] E. Schmidt, *Ber.*, **52**, 409 (1919).

[12] Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927).

[13] Porter, Stewart and Branch, "Methods of Organic Chemistry," Ginn and Co., 1927, p. 182.

[14] J. L. Simonsen, "The Terpenes," Vol. I, Cambridge University Press, London, 1931, p. 60.

[15] Young, Ballou and Nozaki, THIS JOURNAL, **61**, 12 (1939).

[16] Gilman and Kirby, *ibid.*, **54**, 345 (1932).

[17] This analysis was supplied by Dr. Haagen-Smit of the California Institute of Technology, Microchemical Laboratories.

[18] Huntress and Mulliken, "Identification of Pure Organic Compounds, Order 1," John Wiley and Sons, Inc., New York, N. Y., 1941.

Summary

Benzylmagnesium chloride reacts with citronellal to give α-benzyl-citronellol and substance A, a glycol formed from one mole of Grignard reagent and 2 moles of aldehyde.

The structure of A has been determined and it has been shown that the Grignard reagent does not add to the ethylenic double bond as postulated by Rupe.[1a]

A mechanism is suggested to account for the abnormal reaction of benzylmagnesium chloride during the formation of substance A.

LOS ANGELES, CALIF. RECEIVED SEPTEMBER 7, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Reaction of Acetaldehyde with Ethyl Bromide at 400°[1]

BY JACK G. ROOF

The kinetics of the pyrolysis of ethyl bromide has been studied extensively by Daniels and coworkers.[2] The primary step is thought to be the formation of an ethyl free radical and a bromine atom. As an independent method of checking on this primary step a series of experiments was carried out on the liberation of free radicals in ethyl bromide by the photolysis of acetaldehyde and ethyl bromide mixtures[3] at temperatures somewhat below that required to decompose the bromide at an appreciable rate. The experimental facts obtained supported the view that free ethyl radicals are formed in the thermal decomposition of ethyl bromide. In these latter experiments it was found that mixtures of acetaldehyde and ethyl bromide reacted rather rapidly in the dark at 357°, at which temperature acetaldehyde is stable and ethyl bromide decomposes at a very slow rate.

The purpose of the present paper is to describe the results of a further series of experiments on the dark reaction of these two compounds at temperatures near 400° in an apparatus better adapted to thermal reactions than was used previously for this mixture.

Experimental

Chemicals.—Acetaldehyde by Eastman Kodak Co. and ethyl bromide by Merck were used throughout. Each of these was dried over anhydrous cupric sulfate and distilled and sealed off in glass ampules under reduced pressure after the manner previously described.[3]

Apparatus.—A molten lead bath, modeled after that of Daniels,[2] was used as a thermostat. Reactions were carried out in Pyrex vessels. Pressures were measured by means of a thin glass diaphragm[4] used as a null-point instrument in an electrical circuit.

A two-liter glass reservoir, painted black to prevent any light reaction, was attached to the reaction system by means of capillary gates, designed after those of Veltman.[2a] The reservoir was evacuated to a pressure of *ca.* 10^{-4} mm. and warmed by a glow-coil to 60° or higher to aid in outgassing. The sealed reservoir was then cooled and bulblets of the reactants were broken in the reservoir by means of magnetic hammers. This storage vessel was so designed that samples of gas came into contact only with glass while in storage or while being transferred to the reaction vessel. By means of magnetically-operated hammers and tractors one could open the reservoir and let a gas sample into the reaction flask. Momentary heating of two thin-walled capillary goose-necks then sealed off both reservoir and reaction flask independently. The chief advantage of the reservoir was that one could maintain constant composition of reactants while studying the other variables of temperature and pressure over a series of experiments.

A micro-analysis apparatus, essentially that of Blacet and Leighton,[5] was available for analysis of products of the last few experiments. The gaseous products passed through a stopcock and through a trap cooled in dry-ice and were collected in the analytical apparatus by means of a Toepler pump. A lower temperature in the trap would have been desirable, in order to decrease the amount of unchanged reactants being introduced into the analytical apparatus.

Results

A few preliminary experiments were carried out on the pyrolysis of pure ethyl bromide. The plots of pressure *vs.* time were similar to those of Daniels. There were indications of an induction period in the reaction, but the pressures used were higher than those at which this phenomenon is pronounced.[2a]

Twenty-one experiments were then performed on acetaldehyde–ethyl bromide mixtures. A summary of the data is shown in Tables I and II. Pressure–time curves for three typical runs at 404° are shown in Fig. 1. Certain facts are immediately noticeable about these plots. There was a definite induction period of comparatively long duration, with the inflection point not being reached for a matter of minutes. This induction period was quite different from the "time lag" reported for the pyrolysis of ethyl bromide. In this latter case the pressure remained constant for several minutes and then started upward at a continuously decreasing rate as required for a first-order reaction.

For the mixtures there was an abrupt drop-off in the rate of pressure increase after a certain time. This "knee" was followed by a slow pressure rise which decreased in rate over a period of another hour or more, much after the fashion of ethyl bromide alone.

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(1) Published with approval of the Monographs Publications Committee, Oregon State College, Research Paper No. 78, School of Science, Department of Chemistry.

(2) (a) P. Fugassi and F. Daniels, THIS JOURNAL, **60**, 771 (1938); (b) F. Daniels and P. Veltman, *J. Chem. Phys.*, **7**, 756 (1939).

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