hydrocarbon, giving 22 mg. of chrysene as the sole homogeneous product.

1 - (o - Chlorophenyl) - 2 - (α - naphthyl) - propene (X).—An ethereal solution of 3.2 g. of the aldehyde III was added at 0° to the reagent from 4.2 g. of o-chlorobromobenzene and 0.6 g. of magnesium and the temperature was slowly raised from 0° to the boiling point. The product was collected as a viscous oil (5.3 g.) which was heated with 7.5 g. of potassium bisulfate at 170–180° for one hour and distilled twice, giving a light yellow oil, b. p. 150–180° (1 mm.); yield 3.1 g. (64%).

Anal. Calcd. for $C_{19}H_{15}Cl$: C, 81.86; H, 5.42. Found: C, 81.27; H, 5.66.

In various experiments this olefin was refluxed with potassium hydroxide in quinoline for three hours, stirred with potassium hydroxide at 250–260° for seven minutes, or at 250–300° for twenty minutes, but this resulted only in tars or in oils from which no crystalline trinitrobenzene derivative could be isolated. The carbinol was also fused with potassium hydroxide under various conditions without successful result.

When o-bromoiodobenzene was used in the synthesis the distilled carbinol contained only 13.0% of halogen, as compared with the theoretical value of 23.4%. No satisfactory product was obtained on dehydration and alkali fusion.

Summary

A convenient method of preparing 2-(α-naph-
thyl)-propionaldehyde has been found in the condensation of α-naphthylmagnesium bromide with methoxyacetonitrile followed by a methyl Grignard reaction on the resulting methoxymethyl α-naphthyl ketone and acid dehydration of the carbinol. The aldehyde can be reduced smoothly to the alcohol and the latter converted into the chloride.

With these intermediates readily available, an attempt was first made to synthesize 5-methylchrysene by the Bogert–Cook method, but there was obtained instead a hydrocarbon identical with Newman's 6-methylchrysene. Apparently in analogy with the para migration of a methyl group attached to a saturated ring observed by Haworth, an ortho methyl migration occurs in the dehydrogenation.

Various other possible methods of utilizing the same intermediates for the synthesis of 5-methylchrysene were explored without success, the difficulty being associated in part with the ready loss of methyl from the 5-position, as observed by W. E. Jones and Ramage.

Converse Memorial Laboratory
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The Oxygen Effect in the Reaction of Cyclopropane with Bromine and with Hydrogen Bromide

By M. S. Kharasch, M. Z. Fineman and F. R. Mayo

Previous papers from this Laboratory[1–3] have shown that the brominations of toluene and phenanthrene are markedly accelerated by traces of oxygen and peroxides. These and similar observations with other hydrocarbons[4] have led us to reëxamine the reactions of cyclopropane with bromine and with hydrogen bromide.

Previous Work

The literature on the reaction of cyclopropane with bromine and hydrogen bromide is meager, although a great deal of work has been done with substituted cyclopropanes.[5] Gustavson[6] states

(1) Kharasch, Margolis, White and Mayo, This Journal, **59**, 1405 (1937).
(2) Kharasch, White and Mayo, *J. Org. Chem.*, **2**, 574 (1938).
(3) Kharasch, White and Mayo, *ibid.*, **3**, 33 (1938).
(4) Kharasch, Hered and Mayo, unpublished work.
(5) (a) Farmer, *J. Chem. Soc.*, **123**, 3341 (1923); (b) Demjanow and Dojarenko, *Ber.*, **56B**, 2200 (1923); (c) Nicolet and Sattler, This Journal, **49**, 2066 (1927); (d) Bone and Perkin, *J. Chem. Soc.*, **67**, 118 (1895); (e) Gustavson, *J. prakt. Chem.*, [2] **62**, 270 (1900).
(6) Gustavson, *ibid.*, [2] **62**, 273 (1900).

that at ordinary temperatures cyclopropane reacts with bromine quite slowly in the dark, and rapidly in sunlight. He noted that propyl bromide, more highly brominated products, and large quantities of hydrogen bromide were formed in addition to trimethylene bromide. Ogg and Priest[7] have investigated several vapor phase reactions of cyclopropane. At 250° iodine yielded 1,3-diiodopropane and light had no effect on the reaction. At room temperature under intense illumination, bromine added to give mostly 1,3-dibromopropane and a little hydrogen bromide. At 220° in the dark, large proportions of hydrogen bromide were formed. Hydrogen bromide gave little indication of reaction at 300°.

Experimental Part

The cyclopropane used in this work was obtained from the Ohio Chemical Company. It boiled at −33.5 to

(7) Ogg and Priest, This Journal, **60**, 217 (1938).

−33° and was completely absorbed by concentrated sulfuric acid. The method of preparation excluded the possibility of the presence of propylene and similar impurities.[8] Analytical reagent grade bromine was used. It was dried with anhydrous calcium bromide and distilled in an all-glass apparatus. Only the middle fraction which boiled at 58.7° at 751 mm. was used.

Difficulty was experienced in obtaining consistent results in the study of the addition of bromine and hydrogen bromide to cyclopropane until the apparatus shown in Fig. 1 was devised for eliminating dust and water from the reaction.
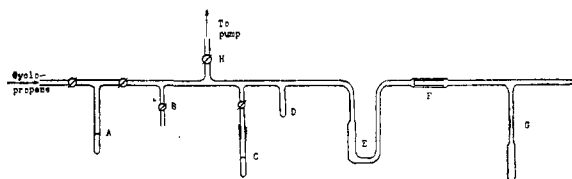

Fig. 1.

A was calibrated to contain 1.56 g. of liquid cyclopropane at the temperature of a solid carbon dioxide–acetone bath. The tube C was calibrated (by titration) to contain 0.288 or 2.62 g. of liquid hydrogen bromide at a similar temperature and was attached to the system through a ground glass connection. To avoid contact of bromine with stopcock and joint lubricant, bromine was weighed out in a tube which was then sealed onto the line at D. After the tube containing hydrogen bromide or bromine was attached to the system, the tube was cooled in liquid nitrogen and the whole system was evacuated to about 10⁻⁵ mm. through the line H. By suitable manipulations of stopcocks, cyclopropane was introduced into A, any excess hydrogen bromide or cyclopropane was removed from the calibrated tubes by cautious evacuation, and the reactants were degassed.[3] They were then distilled successively through phosphorus pentoxide and a glass wool plug in tube E, and finally through glass filter cloth in tube F, into the reaction tube G. Any added substances had been previously placed in G before it was sealed onto the system and kept cold during the above procedures. For experiments in the absence of oxygen (indicated by − in the oxygen column of the tables), the system was then evacuated once more to remove traces of uncondensed gases and tube G was sealed off at the constriction. For experiments in the presence of oxygen, the degassing operation was omitted and oxygen was admitted through stopcock B until its pressure in the line was 22 cm. before tube G was sealed off. Since this tube was at the temperature of liquid nitrogen it was estimated that the oxygen pressure would increase to about one atmosphere at room temperature.

For the dark reaction, the bomb tubes were allowed to stand in an iron pipe at room temperature. In the photochemical studies (indicated by + in the "light" column in the tables) the reaction tubes were immersed in water kept at 20 ± 5° and only the liquid phase was exposed to light from a 300-watt incandescent lamp at a distance of approximately ten centimeters.

(8) Hass, McBee, Hinds and Gluesenkamp, *Ind. Eng. Chem.*, **28**, 1178 (1936).

After reaction, the bomb tube was immersed in liquid nitrogen and opened. A tube was then sealed on so that the low-boiling contents would distil into water or aqueous potassium iodide solution at room temperature. The remainder was washed into the same solution. Unreacted bromine or hydrogen bromide was then determined by titration.

Reaction of Cyclopropane with Bromine.—In Table I are summarized the experiments which

TABLE I

THE ADDITION OF BROMINE TO CYCLOPROPANE[a]

Added substances[b]	Conditions		Reaction time	% reaction[c]	Remarks
	Oxygen	Light			
None	−	−	52 days	13	2% HBr found
None	+	−	53 days	20	2% HBr found
None	−	+	200 hrs.	47	Checked. 8.3% HBr evolved
None	+	+	1.9 hrs.	100	Checked
None*	+	+	2.0 hrs.	100	
Ascaridole, 0.03	−	+	3.2 hrs.	100	
Bz₂O₂, 0.03	−	+	3.5 hrs.	100	
Bz₂O₂, 0.03	+	+	2.1 hrs.	100	
Ethanol, 0.05	+	+	64.0 hrs.	100	
i-AmONO, 0.1	+	+	204 hrs.	37	2% HBr found
Water, 0.1	+	+	1.7 hrs.	100	
Water, 0.1	−	+	76.7 hrs.	100	Checked. Two phases
HBr, 0.1	+	+	2.1 hrs.	100	

[a] In all cases the mole ratio of bromine to cyclopropane was 1:10, except the one marked with an asterisk when it was 1:2. Experiments in concentrated solution were not carried out because bromine seems to act as an inhibitor for chain reactions under such conditions. [b] Quantities expressed in moles per mole of bromine used. [c] Complete reaction was assumed when color faded to a faint yellow tinge.

demonstrate the effect of various substances on the interaction of bromine and cyclopropane. The first two experiments show that the reaction of cyclopropane and bromine in the dark is very slow, and that oxygen has an accelerating effect on the reaction. It is remarkable, however, that in the absence of oxygen the photochemical reaction is extremely slow (47% reaction in two hundred hours), while in the presence of oxygen the reaction is complete in about two hours. Peroxides exert an effect similar to that of oxygen. Another striking observation is the inhibition of the photochemical oxygen-catalyzed reaction by ethyl alcohol and isoamyl nitrite.

Because of the small quantities of materials used in our study, we were unable to isolate any reaction product other than 1,3-dibromopropane. That other materials are formed was indicated by the formation of hydrogen bromide and small quantities of a material boiling lower than 1,3-dibromopropane.

Reaction of Cyclopropane with Hydrogen Bromide.—Two distinct types of reaction mix-

tures were used in the study of the reaction of cyclopropane and hydrogen bromide. In one group of experiments, equimolecular quantities of the reactants were used, in the second, a tenfold excess of cyclopropane. These procedures yielded strikingly different results as shown in Table II.

TABLE II

THE ADDITION OF HYDROGEN BROMIDE TO CYCLOPROPANE

Added substances[a]	Conditions Oxygen	Light	% reaction	Remarks
None[b]	−	−	8	
None[b]	−	+	11, 12	
None[b]	+	−	81	
None[b]	+	+	99, 99	
Bz₂O₂, 0.03[b]	−	+	74	
(C₆H₅)₂NH, 0.03[b]	+	+	91	
Catechol, 0.03[b]	+	+	28, 41, 43[c]	Catechol not completely
Catechol, 0.03[b]	+	−	41, 50[c]	dissolved
Catechol, 0.03[b]	−	+	41, 43[c]	
Water, 0.1[b]	−	−	87	Two phases
None[d]	−	−	55, 66[c]	
None[d]	−	+	70[c]	
None[d]	+	−	67, 73[c]	
None[d]	+	+	74, 76[c]	
Thiocresol, 0.03[d]	−	+	90	Mixture became warm
Catechol, 0.03[d]	−	− ·	97[b]	in a few
Water, 0.03[d]	−	−	94	minutes
Acetic acid, 0.03[d]	−	−	87	

[a] Quantities expressed in moles per mole of hydrogen bromide used. [b] Mole ratio of hydrogen bromide to cyclopropane was 1:10; the reaction time was two hours. [c] Odor of product indicated formation of propyl ether of catechol. [d] Mole ratio of hydrogen bromide to cyclopropane was 1:1; the reaction time was four hours. [e] Addition products combined and found to be n-propyl bromide.

Thus, when excess cyclopropane was used, and oxygen was removed from the system, a slow reaction took place in the dark (8% in two hours), and only a slight increase was observed upon illumination (11% in two hours). However, in the presence of oxygen a tremendous increase in the reaction velocity was noted. Thus, in two hours a yield of 81% of normal propyl bromide was obtained in the dark and nearly 100% in the light. The effect of benzoyl peroxide on the rate of reaction was similar to that of oxygen. Antioxidants appear to overcome partially the accelerating effect of oxygen, but duplicate experiments show that in illuminated reactions in the absence of oxygen, catechol accelerates the reaction. Since water has the same effect (in the dark), it seems likely that catechol may accelerate the reaction by one mechanism while inhibiting it by a second.

On the other hand, when equimolecular quantities of cyclopropane and hydrogen bromide are used, oxygen and illumination have no significant effect on the rate of reaction. Water, acetic acid, thiophenol and catechol accelerate the addition reactions in the absence of oxygen.

Discussion

It is evident from our experiments that pure cyclopropane and pure bromine do not react appreciably in the dark, and only very slowly in the light. The observations recorded in the literature regarding the ring cleavage by bromine must therefore apply to an oxygen-catalyzed photochemical reaction. A careful study of our data indicates that we are dealing with a chain reaction similar to the oxygen-catalyzed photochemical brominations of phenanthrene[2] and toluene.[1,3] In support of this one may cite the following facts: (1) minute amounts of oxygen or peroxides are effective in bringing about a rapid reaction; (2) traces of inhibitors markedly retard the reaction.

The following schematic representation is suggested for the bromination of cyclopropane (a dot is used to represent an unpaired electron)
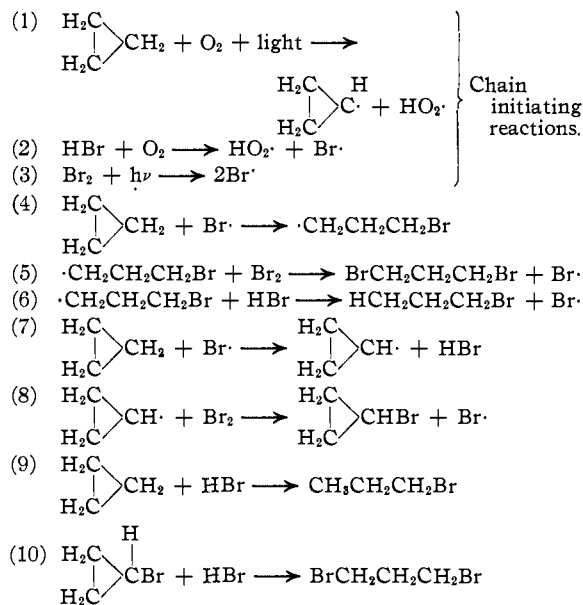
The low-boiling materials observed by us could have been formed in reactions 6, 8 and 9. Reaction 7 readily explains the formation of hydrogen bromide. The relative ineffectiveness of light in the absence of oxygen is surprising for one might expect a fairly large concentration of

bromine atoms from equation 3. This suggests that the active entity responsible for the chain reaction may not be the bromine atom but a free radical of the type ·BrO₂. The latter is a possibility which we are keeping in mind.

From the standpoint of the thesis developed in this paper, an attractive explanation is at once available to account for the fact that cyclopropylamine does not react with bromine, although the ring is easily cloven by nitrous acid.[9] The amino group is an inhibitor in reactions involving bromine atoms. The stability of the ring, therefore, is to be ascribed to the chain-breaking mechanism of the amino group, rather than to the inherently greater stability of the ring in cyclopropylamine. The same explanation applies to the resistance toward cleavage of cyclopropyl cyanide.[5c] The effect of groups on the stability of the cyclopropane ring is, therefore, not necessarily related to ease of cleavage of the ring with bromine.

The oxygen effect in the reaction of hydrogen bromide and cyclopropane, when the latter is used in large excess, is readily correlated with our bromine atom chain mechanism. The free bromine atoms are formed by equations 1 or 2. The formation of normal propyl bromide by the chain mechanism is indicated by equations 4 and 6, by a different mechanism in equation 9.

The ineffectiveness of light and oxygen on the rate of reaction of equimolecular quantities of hydrogen bromide and cyclopropane is suggestive of an ionic mechanism different from an atom or free-radical chain reaction. Furthermore, the fact that substances such as thiocresol, catechol, acetic acid, and water have an accelerating effect lends some support to the idea that the mechanism is ionic in character. These substances are all capable of combining with a proton and thereby causing dissociation of the hydrogen bromide molecule into a bromide ion and a positively charged fragment. The cleavage of the cyclopropane ring by ions would not be expected to be photochemical. The accelerating effect of hydroxylic compounds indicates that the contribution of an atom mechanism to the rate of reaction is insignificant in concentrated hydrogen bromide solutions.

Summary

1. The reaction of bromine with a ten-fold excess of cyclopropane is greatly accelerated by the combined effect of oxygen and light.

2. The reaction of hydrogen bromide with a ten-fold excess of cyclopropane is greatly accelerated by oxygen and only slightly accelerated by light.

3. Organic peroxides have an effect similar to that of oxygen.

4. A chain mechanism involving bromine atoms is suggested for each addition reaction.

5. The addition of hydrogen bromide to an equivalent quantity of cyclopropane is not significantly affected by oxygen or light, but is accelerated by hydroxylic compounds. For this effect a competing non-atomic mechanism is suggested.

(9) Kishner, *Chem. Zentr.*, **72**, 11, 579 (1901); **76**, 1, 1703 (1905).

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Chlorinations with Sulfuryl Chloride. I. The Peroxide-Catalyzed Chlorination of Hydrocarbons

By M. S. Kharasch and Herbert C. Brown[1]

In the past the use of sulfuryl chloride as a chlorinating agent has depended upon the dissociation of the compound, under the experimental conditions, into its components—sulfur dioxide and chlorine. That is, the sulfuryl chloride served as a source of *molecular* chlorine, and it has been used almost exclusively for the chlorination of aromatic nuclei in the presence of halogen carriers.[2]

The utilization of sulfuryl chloride in this way offers little advantage over the use of gaseous chlorine; for this reason sulfuryl chloride has not been generally adopted in the laboratory for carrying out such chlorinations.

In the course of investigations on the chemical properties of free radicals in solution, which are now being carried out in this Laboratory, it was found that in the presence of certain catalysts (such as organic peroxides) sulfuryl chloride can serve as a source of chlorine *atoms*. Using this procedure,

(1) Eli Lilly Fellow, 1938–39.

(2) (a) Tohl and Eberhard, *Ber.*, **26**, 2940 (1893); (b) Silberrad, *J. Chem. Soc.*, **119**, 2029 (1921); (c) **121**, 1015 (1922); (d) Silberrad, Silberrad and Parke, *ibid.*, **127**, 1724 (1925).