this compound. The observed molecular rotation of the cation was very small, and only one form was obtained.

Additional evidence is afforded by the structure reported for pentlandite,[5] (Ni, Fe)S, which places four S atoms about each Ni atom at the corners of a flat pyramid.

In an attempt to test the possibility of a pyramidal configuration for quadrivalent palladium, we have isolated *cis* and *trans* forms of palladium bisantibenzylmethyldioxime. One form is a pale lemon-yellow color with a melting point of 175°, and the other a deeper yellow with a melting point of 207°. Separation of the isomers was effected by fractional crystallization from benzene–petroleum ether solution. The former isomer is readily changed into the latter by boiling in xylene solution for a few minutes, or allowing the benzene solution to stand for a few days. While sodium salts of both forms of palladium bisantibenzylmethyldioxime may be easily prepared, all efforts to obtain brucine, strychnine, and cinchonine salts, and hence all attempts at resolution, have failed. Several more suitable substances suggest themslves: (a) a dioxime containing a salt-forming group, *viz.*, *p*-carboxybenzylmethyldioxime, (b) benzoylpyruvic acid. The latter readily coordinates with palladium and several fairly stable salts of palladobenzoylpyruvic acid have been prepared. Further details regarding the compounds of palladium with benzylmethyldioxime will be published shortly.

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[5] Alsen, "Strukturbericht," Ewald and Hermann (1913–1928), p. 133.

[CONTRIBUTION FROM SOCONY-VACUUM CORPORATION GENERAL LABORATORIES, RESEARCH AND DEVELOPMENT DIVISION, PAULSBORO, NEW JERSEY]

A Contribution to the Chemistry of Cyclopentadiene. I. The Peroxide Effect[1]

BY GEO. R. SCHULTZE[2]

At the beginning of our investigations upon cyclopentadiene and its dimer, difficulties were found in determining the amount of unsaturation by the ordinary methods of bromination. Staudinger and Rheiner[3] have reported that only one double bond is acted upon when cyclopentadiene is brominated under analytical conditions, while the second one is attacked very slowly. However, in no case were values found of 50% which would correspond to the saturation of one double bond. Results between 60 and 90% were obtained for the monomer, and between 105 and 130% for the dimer.

Influence of Air.—The most important result of the present investigation has been the interesting fact that the addition of bromine is affected by the peroxide content of the material. No quantitative results are found whenever the experimental conditions are such as to permit peroxide formation previous to bromination.

The influence of oxygen upon the halogenation of unsaturates has been known for some time. H. Ingle[4] has pointed out the possibility of autoxidation as one of the reasons for incorrect results, but no application of his suggestion apparently has been made. Verhoogen[5] found a variation in the rate of bromination for different gases in contact with the solution. H. S. Davis and co-workers[6] have reported similar effects when acetylenes are titrated with bromine. Geo. R. Schultze[7] has shown that even a bromine-sensitized oxidation of unsaturated hydrocarbons may complicate the quantitative analysis. M. S. Kharasch and co-workers[8] recently have published two papers on the addition of hydrogen bromide to unsaturated compounds which emphasize the fundamental importance of peroxide formation.

After proper precautions were taken to exclude the influence of oxygen, the bromine water titration worked satisfactorily. However, the disturbing influences which caused variations for the results obtained with bromide-bromate according to the method of H. S. Davis[6] were not wholly

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[1] This work was presented at the Washington, D. C., meeting of the American Chemical Society, March, 1933.

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[3] Staudinger and Rheiner, *Helv. Chim. Acta*, **7**, 27 (1924); *cf. Ann.*, **447**, 103 (1926).

[4] Ingle, *J. Soc. Chem. Ind.*, **21**, 587 (1902); **23**, 422 (1904); *Chem. Zentr.*, I, 1401 (1902); II, 504 (1904).

[5] Verhoogen, *Bull. soc. chim. Belg.*, **34**, 434 (1925).

[6] Davis, *et al.*, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 108 (1931).

[7] Schultze, THIS JOURNAL, **53**, 3561 (1931); *Z. angew. Chem.*, **45**, 574 (1932).

[8] Kharasch *et al.*, THIS JOURNAL, **55**, 2468 and 2531 (1933).

removed. They were found to be caused by the presence of acid.

Influence of Acid.—Cyclopentadiene and dicyclopentadiene react explosively when brought into contact with concentrated sulfuric acid.[9] Kraemer and Spilker[10] have reported resinification with dilute acid solutions. It is evident that the use of a 10% acid as required by Davis' method must be detrimental to the hydrocarbons. Only when the acid concentration is lowered to a minimum may accurate values be obtained. *Any method using bromate as an agent to supply free bromine is not fully satisfactory in titrating highly polymerizable material because of the inherent requirement of bromide*[10b] *and acid, both of which favor many polymerizations.* Nevertheless, it was attempted to retain the convenient bromide–bromate method as far as possible. Important modifications were necessary as to the concentrations of the solutions, the order of operations and the time required.

Methods of Titration.—There are two ways of preventing the formation of peroxide. The first is titration in vacuum. The second is titration in presence, initially, of free bromine in excess of the amount required for complete bromination of the hydrocarbons. In the latter case, the titration is possible even in the presence of air, as was proved experimentally. If, however, the capsules containing the compound are broken *before* bromine water is added, or *before* an excess of free bromine is liberated from bromide–bromate, the determination is incomplete because of peroxide formation. The second of the following methods has given the greatest accuracy, but it involves the well-known disadvantages of bromine water when used as standard solution.

(a) **Modified Bromide–Bromate Titration.**—Fifty ml. of sulfuric acid is placed in a vacuum titration bottle. The acid must not be stronger than 0.4 normal (89 ml. of water plus 1 ml. of concd. acid). A glass capsule containing 0.1 to 0.8 g. of sample is inserted, and the bottle is evacuated. Maintaining the vacuum, an excess of bromide–bromate solution is admitted. The bottle is wrapped in black paper and allowed to stand for fifteen minutes in order to permit complete liberation of the free bromine. After this period the capsule is broken by vigorous shaking. After five to twenty minutes of shaking potassium iodide is added, the bottle well shaken for three more minutes, then the vacuum broken and the free iodine back-titrated with thiosulfate using starch as an indicator.

If the bottle is shaken only occasionally, the duration of the experiment should be extended to about ninety minutes. The capsule may be broken before bromide–bromate is added. This is advantageous for cyclopentadiene because the time permitted for spontaneous polymerization is shortened. In this case, however, the color of the free bromine will disappear completely during the first ten minutes since the rate of the liberation of free bromine is considerably slower than that of the bromination reaction.

(b) **Bromine Water Titration.**—A little water is placed in the vacuum bottle. This lowers the possibility of breaking the fragile capsule prematurely and facilitates evacuation. After inserting the capsule, the bottle is evacuated and wrapped in black paper. The air on top of the stopcock is replaced by water and the bottle, by means of a short piece of rubber tubing, connected to the buret which contains a saturated and standardized solution of bromine water. An excess of the solution is admitted, a considerable excess being unharmful, at least for the monomer. Then the capsule is broken. The steps of the procedure thereafter are the same as described above.

(c) **Titration in the Presence of Air.**—After the peroxide effect had been established and frequently substantiated, it was most surprising to find that the titration of both cyclopentadiene and dicyclopentadiene can be made even in the presence of air, provided free bromine is present in excess of the amount required *before* the capsule is broken. No time is permitted in this way for the hydrocarbons to form peroxides since the bromination is a faster reaction.

In these experiments, free bromine was allowed to generate for at least fifteen minutes prior to breaking the capsule. When method 2 was used, the bromine water was added first and then the capsule broken. Oxygen (air) was present during the experiments, yet the bromination is complete. However, the advantages of admitting the volatile free bromine into a vacuum without losses makes the vacuum titration preferable to a change in procedure. Moreover, it is safest to exclude the possibility of peroxide formation by removing the oxygen entirely.

Preparation of the Hydrocarbons

Technical dicyclopentadiene was depolymerized by slow distillation through a column 30 cm. in length, filled with glass beads. The air in the entire system was replaced by nitrogen. During the distillation the receiver communicated with the outside through an atmosphere of nitrogen. It was found later that no polymerization takes place at dry ice temperature of the receiver within four days, even in the presence of air. Only the distillate between 40 and 41° was collected which was found to be pure cyclopentadiene.

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[9] J. Boes, *Chem. Zentr.*, II, 32 (1902).

[10] Kraemer and Spilker, (a) *Ber.*, **29**, 554 (1896); (b) Staudinger and Bruson, *Ann.*, **447**, 117 (1926).

Dicyclopentadiene was prepared in two different ways. First, it was obtained from the monomer by storage for at least four weeks in the dark at about 25°. The sample bottles were filled in complete absence of air and sealed off under vacuum. The second method for obtaining pure dicyclopentadiene was by distillation at 60° under 14 mm. pressure. Description of the apparatus for filling the capsules in an atmosphere of nitrogen immediately before each analysis must be omitted for the sake of brevity.

Results

For cyclopentadiene the three methods give equally good results. No threshold is found for the saturation of one double bond. In fact, the bromination reaches more than 95% within the first two to three minutes. The limits of error average ± 0.6% with one maximum deviation of 2% for more than thirty experiments.

The quantitative determination of the dimer involves considerably more difficulties than the titration of the monomer, and check experiments should generally be run. The experimental conditions are more limited than for the monomer. A large excess of halogen should be avoided. The temperature should be adjusted between 30 and 35°. The time of bromination in general should not be longer than ten minutes. While for cyclopentadiene the capsules may be broken first and then the halogen added, the inverted order is the better practice for dicyclopentadiene. For titration in presence of air the latter procedure must be used. In titrating the dimer, method 1 is distinctly inferior to methods 2 and 3. It gives values generally 6 to 7% above the theoretical value while the limits of error are about 2% for the methods 2 and 3. A time as short as three minutes is sufficient to ensure an almost complete bromination. On the other hand, the amount of bromine used up does not increase appreciably when the time is extended to about fifteen minutes. For longer than thirty minutes, substitution of hydrogen becomes very distinct, which is in contrast to the behavior of the monomer where no further bromination occurs.[11] The experimental data are omitted for the sake of brevity.

It may be recalled that at room temperature cyclopentadiene is not a stable compound. It polymerizes at a rather rapid rate, the dimer being the only product of reaction. The determination of the degree of polymerization thus becomes a matter of analyzing mixtures of cyclopentadiene and dicyclopentadiene. Since previous experience had proved that bromine water was superior to bromide–bromate in titrating the dimer, only method 2 was used in analyzing the mixtures. These were either synthetical or natural mixtures formed by permitting the monomer to polymerize for different lengths of time. The degree of polymerization X, *i. e.*, the fraction of the dimer in the mixture of monomer and dimer ($100X = \%$), may be calculated from the formula

$$X = 2 - \frac{66.05qN}{2000W}$$

where q is the number of ml. of bromine solution of the normality N, and W is the number of grams of the sample. Table I illustrates the results.

TABLE I

ANALYSIS OF MIXTURES OF CYCLOPENTADIENE AND DICYCLOPENTADIENE

Expt.	Duration in min.	n^{25}_D	Degree of polymerization in % Calcd. from refr. index	Found from titration
1	10	1.4760	48.9	48.7
2	15	1.4768	50.1	49.9
3	15	1.4768	50.1	52.9
4	20	1.4463	5.8	6.5

The results were checked by means of the refractive index. Straight-line interpolation was applied between the values for 100% cyclopentadiene and 100% dicyclopentadiene. The titration indicates that there are no great deviations from the linear relation between the index of refraction and the concentration. Since by the use of the above equation an accurate method is available which, for comparison, gives a true indication of the degree of polymerization, it should be possible to apply, to the system under test, Zawidsky's method of correction for binary systems.[12] Stobbe and Reuss[13] have already considered this possibility but no definite assertion was possible at that time since no correct method existed for the evaluation of the change in the index of refraction. The polymerization of cyclopentadiene and its relation to the index of refraction will be dealt with in a later publication.

Criteria of Accuracy.—The following facts have been established which may serve as reliable indications for the normal course of bromination.

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[11] *Cf.* Roscoe, *Ann.*, **232**, 349 (1886); J. Thiele, *ibid.*, **314**, 296 (1901); Kraemer and Spilker, *loc. cit.*, p. 556.

[12] Zawidsky, *Z. physik. Chem.*, **35**, 140 (1900).

[13] Stobbe and Reuss, *Ann.*, **391**, 154 (1912).

(a) In the case of cyclopentadiene, the products of bromination will be completely soluble[14] in the solution. Any precipitate should be white or slightly yellow.

(b) The end-point of the thiosulfate titration should be definite. If the blue color of the starch–iodine complex returns within three minutes, good results cannot be expected.

(c) If dicyclopentadiene is present, the bromination products are more complex in nature. The slow progression of the polymerization of the brominated material is evidenced by its change in color from yellow-white, through green to dark blue or black. All these colors may appear without noticeable effect upon the completeness of bromination. Therefore, this polymerization seems to be a secondary reaction after the bromination has taken place. The final product will usually be a very viscous resin. If the product is a purple liquid, the results are not quantitative.

Catalytic Influences.—The elimination of catalysts, *i. e.*, certain minute traces of impurities, is very difficult. The criteria mentioned above are the best indications for the presence of catalysts which cause irregularities. When potassium bromide is added to the bromine water in order to lower its volatility and to effect greater concentrations of bromine, low bromination values are found consistently. Potassium bromide acts as a catalyst for increasing the rate of polymerization, which tends to decrease the yield of bromination.[10b] From this point of view it must be considered as an exception that the titration of at least the monomer can be achieved with bromide–bromate, *i. e.*, in the presence of potassium bromide. The effect is rather minute and would not be emphasized, were it not for the fact that it is aggravated by the use of solvents.

The influence of acid has been dealt with before. It cannot be excluded entirely as long as bromide–bromate solution is used, but it appeared that Davis' suggestion[6] of adding the acid slowly to the olefin in the presence of bromide–bromate might be advantageous. The attempt failed, although 0.4 normal acid was used. By using method 2 and adding acid to the system, all the other disadvantages which may be inherent in method 1 are eliminated. Yet incorrect results were obtained.

Action of Peroxide.—The peroxide effect is best explained by the assumption of a chain mechanism for the bromination of cyclopentadiene and its dimer. Only in this manner is it conceivable that minute traces of peroxide have such an enormous effect upon the bromination. Suggestion of a reaction mechanism will be reserved for a future publication when more specific data about the kinetics of the reaction are available.

For cyclopentadiene, two further possibilities of explaining the deficiency of bromination were investigated with negative results. First, the occupation of a double bond by oxygen may actually block the addition of bromine. If this is the case, the deficiency of the bromine absorbed should be represented by, or at least proportional to, the oxygen absorbed. Actually, oxygen is absorbed at a slow rate. On the other hand, the peroxide effect becomes apparent after less than one-half of one minute, when only infinitesimal amounts of oxygen are absorbed. This fact lends strong support to the assumption of a chain reaction.

Second, it is known that cyclopentadiene polymerizes freely at room temperature. Accordingly the bromination number drops rapidly. If polymerization should be accelerated by oxygen, the discrepancy between the theoretical and actual bromination numbers might be explained. The references of the literature are somewhat contradictory.[15] Therefore, samples of freshly prepared cyclopentadiene were sealed in the presence of oxygen (air) and *in vacuo*. Only minute differences in the degree of polymerization were detected (titration and refractive index) after one-half to eight hours which were by far too small to explain the effect. However, the experiments justify the important conclusion that the polymerization of cyclopentadiene is independent of the presence of oxygen (peroxide).

Summary

1. Cyclopentadiene and dicyclopentadiene absorb oxygen (from the air) within a very short time to such an extent that the quantitative bromination of these hydrocarbons is prevented. Minute traces have an enormous influence, and a chain mechanism must be assumed to explain the effect.

2. The spontaneous polymerization of cyclopentadiene to its dimer is practically independent of the presence of oxygen and peroxide.

3. The quantitative bromination of the two double bonds of these compounds can be arrived

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[14] *Cf.* Kraemer and Spilker, and Spilker, *Ber.*, **29**, 556 (1896).

[15] Staudinger and Lautenschlaeger, *Ann.*, **488**, 6 (1931); Stobbe and Reuss, *ibid.*, **391**, 151 (1912).

at by titrating either *in vacuo* or in the presence of an excess of free bromine from the very beginning of the test. Three methods of analysis are described in detail, and criteria are presented for a normal course of bromination.

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

The Knoevenagel Reaction and the Synthesis of Unsaturated Nitro Compounds

BY DAVID E. WORRALL

It has long been known that organic bases may be used to condense aldehydes with substances containing an active methylene group, yet the role played by the amines is still obscure. The explanation offered by Knoevenagel and others of the intermediate formation of a Schiff base does not account for the activity of tertiary amines as Hann and Lapworth[1] have pointed out. These investigators proposed a hypothesis in which the base is assumed to function by lowering the concentration of hydrogen ions, through the formation of small amounts of an ammonium derivative, thereby facilitating dissociation of the tautomeric substance. The ammonium salt or the dissociated enol reacts with the aldehyde forming a β-hydroxy derivative that is unstable, spontaneously changing into an unsaturated compound through the loss of water. They showed experimentally with acetoacetic ester that tertiary amines are effective, but were unable to isolate the intermediate derivatives. The nitro series offers a more promising field in a study of the mechanism of this reaction, for the corresponding derivatives are more stable. Phenylnitroalcohol, $C_6H_5CHOHCH_2NO_2$(1), for example, has been isolated.[2] Accordingly, the action of various amines on nitromethane has been investigated despite the fact that Knoevenagel and Walter[3] obtained unsaturated compounds and recorded that primary amines only were effective.

It has now been found in accordance with Haworth's views that nitromethane and benzaldehyde condense under the influence of diethyl and triethylamines, forming I. A similar reaction takes place with the primary aliphatic amines and the production of nitrostyrene (II) is due to secondary effects. When an amine is added to the above mixture it reacts with water, normally present to some extent, forming an ammonium base. The base tends to react with the acidic enol, thus promoting dissociation of the latter and therefore its addition to the aldehyde.

$$\text{Amine} + H_2O \rightleftarrows \text{Amine H}^+ + OH^-$$
$$\text{Amine H}^+ + OH^- + CH_2NOO^- + H^+ \leftrightarrows CH_2NOO\ \text{amine H} + H_2O$$

Accordingly, it is not surprising that the reaction may be strongly repressed by avoiding the presence of water. No further changes result with a tertiary amine.

The effect of a primary amine is apparently entirely different. A Schiff base is formed even with small amounts of the organic base while the final product is II. This suggests the formation of an addition product of nitromethane with the Schiff base, followed by decomposition into II and the amine. But such an addition product containing an aliphatic amine has never been isolated. Moreover, the assumption is unnecessary as I decomposes in the presence of primary aliphatic amines into nitrostyrene and water. The real function of the Schiff base is to furnish through hydrolysis a small amount of free base which then reacts like triethylamine in causing the formation of I. The latter substance then decomposes into II. The reaction takes place much more slowly than with a tertiary amine and the mixture will stand the application of heat, precisely the effects one would predict from the smaller concentration of available amine.

Secondary amines react less rapidly and less completely with aldehydes and therefore are more destructive. They are the least suitable of the amines for the synthesis of unsaturated nitro compounds.

o-Chloro and *m*-nitrobenzaldehydes react much more readily than benzaldehyde with nitromethane, provided triethylamine is present. The reaction, on the contrary, is sluggish with a primary amine. The acidic character of the molecule is increased in these substituted benzalde-

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(1) Hann and Lapworth, *J. Chem. Soc.*, **85**, 46 (1904).

(2) Holleman, *Rec. trav. chim.*, **23**, 299 (1904).

(3) Knoevenagel and Walter, *Ber.*, **37**, 4503 (1904).