*Anal.* Calcd. for $C_{33}H_{52}O$: C, 85.28; H, 11.28; O, 3.44. Found: C, 85.50; H, 11.28; 0, 3.59.

**$\Delta^2$-3-Phenylcholestene (III).**—A mixture of 1.0 g. of pure II, 10 ml. of pyridine and 1.3 ml. of thionyl chloride was maintained at ice-bath temperature for 3 minutes. Following dilution with water (30 ml.) the solution was extracted three times with 50 ml. of chloroform. After being washed with dilute acid, aqueous sodium bicarbonate and finally with water, the extract was dried and evaporated. By these means there was obtained 0.80 g. of oily crystals which following several recrystallizations from acetone yielded 0.50 g. of III, m.p. 126–127°, $[\alpha]_D$ +53°, $\lambda_{max}^{EtOH}$ 248–250 m$\mu$, log $\epsilon$ 4.04.

*Anal.* Calcd. for $C_{33}H_{50}$: C, 88.72; H, 11.28. Found: C, 88.98; H, 11.20.

In exactly the same manner there was obtained from 1.1 g. of pure V, 0.35 g. of III, m.p. 125–126°, identical in all respects with that material isolated above.

**2$\alpha$,3$\alpha$-Oxido-3$\beta$-phenylcholestane (IV).**—A solution of chloroform (100 ml.) and 1.3 g. of $\Delta^2$-3-phenylcholestene (III) was cooled to 0° and then treated with 275 ml. of 0.5 *N* ethereal monoperphthalic acid. The resulting mixture was maintained at 5° overnight whereafter it was washed consecutively with 5% aqueous sodium bicarbonate and water. After drying and evaporation there was obtained 1.2 g. of crystals, m.p. 113–115°, which were readily recrystallized from acetone to a constant melting point, m.p. 133–135°, $[\alpha]_D$ +63°; $\lambda_{max}^{EtOH}$ 252–254 and 258–260 m$\mu$, log $\epsilon$ 2.40 and 2.40.

*Anal.* Calcd. for $C_{33}H_{50}O$: C, 85.65; H, 10.89; 0, 3.46. Found: C, 85.31; H, 11.05; 0, 3.63.

**3$\beta$-Phenylcholestane-3$\alpha$-ol (V).**—Tetrahydrofuran (60 ml.) containing 0.61 g. of epoxide IV and 1.0 g. of lithium aluminum hydride was heated at reflux temperature for 20 hours with constant stirring. The mixture was then decomposed by the cautious addition of saturated aqueous sodium sulfate followed by solid sodium sulfate. Filtration and evaporation provided a non-crystalline residue which was then chromatographed over 20 g. of alumina. Elution with hexane provided material (0.32 g.) which after several recrystallizations from acetone yielded authentic V, m.p. 161–163°, identical in all respects with V obtained by the action of phenylmagnesium bromide on cholestan-3-one (I); *vide supra*.

**3$\beta$-Phenylcholestane (VI).** A. **By the Action of Raney Nickel on 3$\alpha$-Phenylcholestan-3$\beta$-ol (II).**— A mixture of 0.20 g. of II and 3 g. of Raney nickel in 25 ml. of ethanol was heated for 3 hours at reflux temperature. After this period the solution was filtered through Celite and the filter cake was copiously washed with hot ethanol. Evaporation of the combined filtrates provided a residue which crystallized from acetone to provide 90 mg. of crystalline VI, m.p. 105–109°, obtained pure following one recrystallization from the same solvent; m.p. 113–114°, $[\alpha]_D$ +31°, $\lambda_{max}^{EtOH}$ 254, 258–260 and 268 m$\mu$; log $\epsilon$ 2.28, 2.33 and 2.22.

*Anal.* Calcd. for $C_{33}H_{50}$: C, 88.72; H, 11.28. Found: C, 88.62; H, 11.53.

B. **By the Action of Raney Nickel on 3$\beta$-Phenylcholestan-3$\alpha$-ol (V).**—In an experiment conducted exactly as above in A, 0.20 g. of V led to the isolation of 80 mg. of slightly impure VI, m.p. 108–111°. A single recrystallization from acetone then yielded material identical in all respects to that isolated in A.

C. **By Catalytic Reduction of $\Delta^2$-3-Phenylcholestene (III).**—To 10 ml. of ethyl acetate containing 10 mg. of prereduced 5% palladium-on-charcoal was added 26 mg. of III in 10 ml. of ethyl acetate. The hydrogen uptake was not measured but after 2 hours of stirring in a hydrogen atmosphere the mixture was filtered. Evaporation to dryness followed by a single crystallization from acetone provided 12 mg. of VI, m.p. 112–113°, identical with the material isolated in part A.

D. **By Li/NH$_3$ Reduction of $\Delta^2$-3-Phenylcholestene (III).**—Tetrahydrofuran (2 ml.) containing 75 mg. of III was added with stirring to a solution of 0.10 g. of lithium in 20 ml. of liquid ammonia. After 1 minute of stirring the blue color of the solution was discharged by the addition of a few drops of methanol. Following evaporation to dryness the residue was triturated with hexane and the hexane was then passed through 2 g. of alumina. From the first fractions there was obtained 60 mg. of crystals, m.p. 103–106°, which after one recrystallization from acetone provided 28 mg. of VI, m.p. 113–114°, identical in all respects with the material isolated above in A.

**Treatment of 3$\beta$-Phenylcholestane-3$\alpha$-ol (V) with Pyridine–Chromium Trioxide.**—To 0.6 ml. of pyridine containing 33 mg. chromium trioxide was added 33 mg. of V. After 20 hours at room temperature the mixture was diluted with ethyl acetate (3 ml.) and filtered through 2 g. of alumina. Elution of the column with ethyl acetate provided in the first fraction *ca.* 20 mg. of a slightly colored crystalline residue. Following three triturations with 0.3 ml. of acetone there was obtained 15 mg. of colorless crystals, m.p. 161–163°. A mixed melting point with authentic 3$\beta$-phenylcholestane-3$\alpha$-ol (V) of the same melting point was not depressed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE 5, WASH.]

# Cyclopropene. V. Some Reactions of Cyclopropene[1]

BY KENNETH B. WIBERG AND WILLIAM J. BARTLEY

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A number of the reactions of cyclopropene, including the addition of bromine, iodine and similar reagents, the thermal rearrangement, polymerization, formation of argentic complex, addition of diazo compounds and reaction with dienes are discussed. An estimate of the heat of formation is made, and is used in interpreting the results of the investigation.

Because of the interesting structure of cyclopropene and our interest in the effects of bond angle deformation on the reactions and properties of organic compounds, we have examined a number of the reactions and properties of cyclopropene. The ones to be discussed here are those which bear on the thermodynamic destabilization of cyclopropene as compared to cyclopropane.

**Thermal Rearrangement.**—One of the more informative reactions of cyclopropene is the thermal isomerization to methylacetylene. When a stream of cyclopropene mixed with helium is passed through a glass tube packed with glass helices at 325° (600°K.), rearrangement proceeds slowly. At 425°, the rearrangement is fairly rapid.[2] In a typical experiment, the effluent gas contained methylacetylene and cyclopropene in the ratio of 5:1. Under the same conditions, methylacetylene did not give a detectable amount of cyclopropene. Thus, the equilibrium constant for the reaction is at least 30,[3] and the free energy of isomerization is less than −4.7 kcal./mole.

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(1) This work was supported by the Office of Ordnance Research, U. S. Army.

(2) This rearrangement has also been observed by Dr. F. P. Lossing, National Research Council, Canada.

(3) One per cent. of cyclopropene in the mixture could be detected and 3% could easily be seen in the infrared spectrum.

The quantity of primary interest is the enthalpy of rearrangement. In order to obtain this, and to correct it to 25°, it is necessary to have the free energy and enthalpy functions and the entropy of both methylacetylene and cyclopropene. The values for the former have been tabulated.[4] The availability of accurate values for the moments of inertia of cyclopropene,[5] ($I_A = 2.792 \times 10^{-39}$ g. cm.$^2$, $I_B = 3.846 \times 10^{-39}$, $I_C = 6.085 \times 10^{-39}$) and an assignment for the vibrational frequencies,[6] permit the calculation of the thermodynamic functions for this compound. The values are given in Table I.

TABLE I

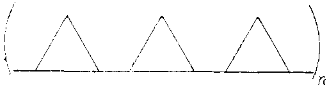
THERMODYNAMIC FUNCTIONS FOR CYCLOPROPENE AND METHYLACETYLENE

| $T$, °K. | $(F^0 - H^0_0)/T$ | $(H^0 - H^0_0)/T$ | $S^0$ |
|---|---|---|---|
| | Cyclopropene | | |
| 298.1 | −49.15 | 9.23 | 58.38 |
| 300 | −49.21 | 9.25 | 58.46 |
| 400 | −52.03 | 10.51 | 62.54 |
| 500 | −54.52 | 11.89 | 66.41 |
| 600 | −56.82 | 13.24 | 70.06 |
| 700 | −58.95 | 14.50 | 73.45 |
| | Methylacetylene | | |
| 298.1 | −48.89 | 10.41 | 59.30 |
| 600 | −57.44 | 14.44 | 71.88 |
| 700 | −59.76 | 15.62 | 75.38 |

It can be seen that at 700°K. the entropy of isomerization is +1.9 e.u., and therefore the enthalpy of isomerization at 700°K. is less than −3.4 kcal./mole. The value at 25° will be the same. This value may be compared with that for the cyclopropane-propylene rearrangement which is −7.9 kcal./mole.[7]

The heat of formation of methylacetylene is 44.3 kcal./mole.[4] This combined with the above value gives a minimum heat of formation of cyclopropene of 47.7 kcal./mole. The heat of hydrogenation to cyclopropane would be less than −35 kcal./mole. The hydrogenation of cyclopentene to cyclopentane generates similar (but less severe) hydrogen repulsions in the product as in the cyclopropene–cyclopropane case. The heat of hydrogenation of cyclopentene is −26.6 kcal./mole,[4] and the difference between this value and that for cyclopropene will be a measure of the extra strain energy in the latter as compared to cyclopropane. The value of this quantity is then at least 8 kcal./mole and possibly considerably greater. This degree of destabilization should be reflected in the reactions of cyclopropene, and the following studies are directed toward exploring this possibility.

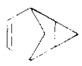
**Polymerization.**—Unlike other simple alkenes, cyclopropene polymerizes spontaneously. It is stable indefinitely as a solid at liquid nitrogen temperature, it polymerizes slowly at Dry Ice–acetone temperature, and on attempted fractional distillation at −36° (its boiling point at atmospheric pressure), the majority of the material was lost as the polymer. At about −10° it may be kept for some time in a dilute carbon tetrachloride solution, but at room temperature the polymerization occurs readily. The structure of the polymer is clearly shown by the n.m.r. spectrum. No vinyl or ordinary methylene proton resonance is observed, but rather there is a broad band at $\tau$ = 9.7–9.8.[8] This can result only from the protons attached to a cyclopropane ring, and thus the structure must be that of a polycyclopropene



It would seem reasonable to assume that the polymerization under the above conditions is a free radical chain reaction. Simple alkenes do not readily polymerize by this type of process for two reasons. First, hydrogen abstraction from the allylic position of the monomer may occur leading to degradative chain transfer.[9] Second, it appears that the radicals formed by addition of the growing chain are stabilized by substituents to a greater degree than are the monomers,[10] and thus the rates of reaction of the simple alkenes are much lower than that of those having groups which may stabilize the radical by conjugation. With cyclopropene, a simple LCAO-MO calculation suggests that the resonance stabilization of the cyclopropenyl radical will be comparable to an allyl radical. However, in view of the higher activation energy for hydrogen abstraction from cyclopropane compared to ordinary methylene groups,[11] it is probable that the activation energy for the abstraction of a hydrogen from cyclopropene will be greater than that for an allylic hydrogen and thus chain transfer should be less important than for the latter.

Further, the additional strain energy in cyclopropene will be relieved on addition of a growing chain, and this should make cyclopropene markedly more reactive than other alkenes in this type of polymerization. Thus the two factors both operate in the favor of ready polymerization of this compound.

**Diels-Alder Reaction.**—In view of the additional strain energy of cyclopropene, it might be expected to act as a dienophile. This has been verified by examining its reaction with cyclopentadiene and with butadiene. When a mixture of nitrogen and cyclopropene was passed into a cold (0°) solution of cyclopentadiene in methylene chloride, most of the cyclopropene was absorbed, and 97% of the theoretical amount of the adduct was formed. Its structure would be expected to be



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(4) American Petroleum Institute Project 44, Carnegie Institute of Technology, "Selected Values of Properties of Hydrocarbons," Tables No. 12p, 12s, 12t and 12u.

(5) P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959).

(6) D. F. Eggers, Jr., J. W. Schultz, K. B. Wiberg, E. Wagner, L. M. Jackman and R. L. Erskine, to be published.

(7) J. W. Knowlton and F. D. Rossini, *J. Res. Natl. Bur. Standards*, **43**, 113 (1949).

(8) $\tau = 10.00 - \delta^{\text{int}}\text{Me}_4\text{Si}$; G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(9) P. D. Bartlett and R. Altschul, THIS JOURNAL, **67**, 812, 816 (1945).

(10) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 121.

(11) J. R. McNesby and A. S. Gordon, THIS JOURNAL, **79**, 825 (1957).

Evidence for this structure may be found in the observation of proton nuclear resonance absorption at $\tau = 9.63$ indicating that a cyclopropane ring was present. The spectrum also indicated two vinyl protons at $\tau = 4.36$ (for norbornene, these appear at $\tau = 4.06$).

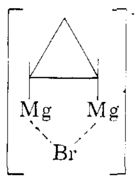
A compound having this structure has been prepared by Simmons and Smith[12] by the reaction between bicycloheptadiene and the iodozincmethyl iodide reagent. This latter compound presumably has the *exo* configuration for the cyclopropane ring since it would be formed by attack from the direction of least steric hindrance.[12] The compound formed in the Diels–Alder reaction might be expected to have the *endo* configuration in view of the general stereochemical results of this type of reaction.[13] The compounds formed by the two methods have been compared, and have been found to be significantly different both in their infrared and n.m.r. spectra. Thus it appears that they are the *endo* and *exo* isomers. The compounds are of interest in that they provide a means of examining cyclopropyl participation in reactions leading to a cationic species at the site of the double bond. These studies are currently in progress.

The fact that cyclopropene reacts readily with cyclopentadiene at a low temperature is in striking contrast to the reaction of ethylene which requires an elevated temperature (190–200°) and a high pressure.[14] The conditions required for the reaction resemble those used with maleic anhydride, one of the more reactive dienophiles. For comparison, we have also examined the reaction with a less reactive diene, butadiene. Here the reaction proceeded less readily, and only a 37% yield of the adduct was formed. The adduct was shown to be $\Delta^3$-norcarene by its n.m.r. spectrum (cyclopropyl protons at 9.64 and vinyl protons at 4.50) and by its hydrogenation to norcarane.

**Addition of Halogen.**—Cyclopropene, like most alkenes, readily adds bromine to form a dibromide. The dibromide was indicated to have the *trans* configuration by the n.m.r. spectrum which had two triplets of equal intensity, one at $\tau = 6.90$ and the other at $\tau = 8.53$. The former corresponds to the protons attached to the carbons bearing the bromines, and the latter must be attributed to the methylene group. If the bromines were *cis*, the two methylene hydrogens would have had different environments and would therefore have different chemical shifts. Since this was not the case, the two bromines must be *trans*.[15]

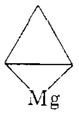
The diiodide is also readily formed by the reaction of cyclopropene with iodine in carbon tetrachloride solution. The increased strain in cyclopropene is manifested in the stability of the diiodide. Ethylene diiodide, for example, reacts rapidly with iodide ion to give ethylene and the triiodide ion.[16] The 1,2-diiodocyclopropene, on the other hand, does not react with iodide ion or with zinc.

The dibromide is particularly interesting in that it appears to be the only simple dibromide which will form a di-Grignard reagent.[17] In connection with our earlier interest in preparing *cis*- and *trans*-cyclopropane-1,2-$d_2$,[18] the Grignard reagent was treated with deuterium oxide. The product was *cis*-cyclopropane-1,2-$d_2$ rather than the expected *trans* isomer. Similarly, when the Grignard reagent was carbonated, the acid isolated was *cis* cyclopropane-1,2-dicarboxylic acid. This suggests that the Grignard reagent may be formulated as



where the magnesiums and the bromine are associated in a way similar to an ion-triplet or where there may be some covalent character to the association. In either way, the association would lead to stabilization of the *cis* configuration.

Recently it has been observed that diethylmagnesium does not exchange magnesium with labeled magnesium bromide,[19] and in view of the fact that magnesium bromide may be precipitated from Grignard reagent solutions by the addition of dioxane, this implies that the Grignard reagent is usually in the form of a dialkylmagnesium. Thus, the Grignard reagent derived from dibromocyclopropane may have the structure



In any event the above facts, coupled with the observation of racemization during the formation of the Grignard reagent,[20] indicates that the *cis* configuration of the Grignard reagent results during the reaction by which it is formed, rather than by an equilibrium process, and that the reaction with water and with carbon dioxide is stereospecific.

**Argentic Complex.**—Traynham[21] has shown that the formation constants for the complex between cycloalkenes and silver ion increases with increasing strain in the alkene. For example, the constants for cyclohexene, cyclopentene and bicycloheptene are 0.0188, 0.114 and 0.270, respectively. The considerably increased strain in cyclopropene should then lead to a markedly higher formation constant for the argentic complex of this hydrocarbon. Cyclopropene was quantitatively removed from a mixture with nitrogen when passed through an aqueous silver nitrate solution. After a short time, the solution began to deposit a black precipitate. The latter was filtered and treated

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(12) H. E. Simmons and R. D. Smith, THIS JOURNAL, **81**, 4256 (1959).

(13) K. Alder and G. Stein, *Angew Chem.*, **50**, 510 (1937); K. Alder and E. Windemuth, *Ber.*, **71**, 1939 (1938).

(14) L. M. Joshel and L. W. Butz, THIS JOURNAL, **63**, 3350 (1941).

(15) *Cf.* the example of the *cis* and *trans* isomers of dimethyl 2,2-diethyloxetane-1,3-dicarboxylate: K. B. Wiberg and H. E. Holmquist, *J. Org. Chem.*, **24**, 578 (1959).

(16) A. Slator, *J. Chem. Soc.*, **85**, 1697 (1904).

(17) Private communication, Professor J. D. Roberts.

(18) B. S. Rabinovitch, E. W. Schlag and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(19) R. E. Dessy, G. S. Handler, J. H. Wotiz and C. A. Hollingsworth, THIS JOURNAL, **79**, 3476 (1957).

(20) C. W. Porter, *ibid.*, **57**, 1436 (1935).

(21) J. G. Traynham and M. F. Sehnert, THIS JOURNAL, **78**, 4024 (1956).

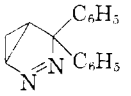
with 30% perchloric acid solution. Most of the precipitate dissolved with the liberation of a yellow-white gummy material. The precipitate is therefore not largely metallic silver since the latter (for example, silver formed from the Tollens reagent and an aldehyde) is not soluble in 30% perchloric acid. The gummy material was found to be insoluble in all common solvents, and therefore was not further investigated. The argentic complex which is probably first formed therefore appears to be unstable, and leads to the formation of a polymeric material.

One way in which to obtain an estimate of the formation constant for this argentic complex involves the competition with other species for silver ion. The ammonium complex has a much larger formation constant ($1.6 \times 10^7$)[22] than the argentic complexes with alkenes, and the latter may be liberated from the solution in aqueous silver nitrate by the addition of ammonia. Cyclopropene, on the other hand, is quantitatively removed from a mixture with nitrogen by an ammoniacal silver nitrate solution. Thus, the cyclopropene argentic complex must have a formation constant on the order of $10^7$. An increase in formation constant from that of cyclopentene by a factor of about $10^8$ would correspond to a difference in free energy of formation of about 11 kcal./mole, which is comparable to the value calculated as the minimum destabilization of cyclopropene as compared to cyclopropane. These numbers have little quantitative significance, but simply indicate that a large amount of the extra strain in cyclopropene is relieved in forming the argentic complex.

The solution of cyclopropene in an ammoniacal silver solution also deposited a black solid on standing for a short time, and again most of the precipitate was found to be soluble in 30% perchloric acid with the liberation of the yellow-white gum.

**Reaction with Diazo Compounds.**—The reaction of cyclopropene with diazo compounds is of interest both with regard to the compounds which may be formed, particularly if a carbene-type reaction may be effected, and with regard to the reactivity of cyclopropene in this type of addition reaction. The reaction with diphenyldiazomethane[23] proceeds readily to give a 1:1 addition compound, even in the presence of copper powder. The addition compound was found to be neutral, and on oxidation with alkaline permanganate it gave benzophenone indicating that the two phenyl groups were still attached to the same carbon. The ultraviolet spectrum had $\lambda_{max}$ 334 mμ (ε 700), 260 mμ (ε 1800) with shoulders at 270, 264 and 254 mμ, and 208 mμ (ε 20,400). The band at 260 mμ is characteristic of the diphenylmethine group. The low intensity band at 334 mμ suggests the presence of a nitrogen-nitrogen double bond. The band at 208 mμ may arise from a group such as —C=C—N=N—. The infrared spectrum did not have an N-H band in the 3μ region.

The structure of the initial addition product may have been I, but the absence of an n.m.r. band above τ = 9 in the isolated product indicated the absence of a cyclopropyl ring. Of the two remaining possibilities (II and III), structure III would seem to better account for the ultraviolet spectrum.



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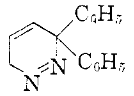
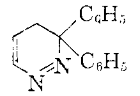


II



III

The reaction with diazoacetic ester proceeded readily at temperatures as low as −40°.[24] The product was a 1:1 addition compound and had an N-H band in the infrared spectrum. Evidently, the addition occurred in a fashion similar to that above, giving a six-membered unsaturated ring.

**Preparation of Cyclopropene.**—The method normally employed for the preparation of cyclopropene involves the pyrolysis of cyclopropyltrimethylammonium hydroxide at 320° using platinized asbestos as the catalyst.[25] This leads to about equal amounts of cyclopropene and cyclopropyldimethylamine contaminated with some dimethyl ether and ethylene. The amine is removed from the gas stream with dilute hydrochloric acid solution, and the other products are separated by vapor phase chromatography over nitrobenzene-Celite.

In the absence of platinized asbestos, the reaction leads to no cyclopropene, and cyclopropyldimethylamine is the only major product. Thus the reaction is of the type observed with phenyltrimethylammonium hydroxide, displacement on methyl.[26] The mode of catalysis by platinized asbestos is not understood.

An attractive alternate to the Hofmann elimination is the pyrolysis of amine oxides, a reaction which works well for the preparation of cyclobutene.[27] When this reaction was attempted with cyclopropyldimethylamine oxide, no cyclopropene was obtained, and the main product was cyclopropyldimethylamine. As an alternate to elimination, degradation to a secondary amine and formaldehyde often occurs.[28] However, the formation of a tertiary amine under these conditions is not a common observation. Since this reaction failed to give cyclopropene, it was not further investigated.

Another potential method for the preparation of cyclopropene involves the Alder-Rickert cleavage of the Diels-Alder adduct formed from cycloheptatriene and dimethyl acetylenedicarboxylate. Alder and Jacobs[29] found that the adduct had the structure derived from the isomeric norcaradiene, and that the cleavage gave dimethyl phthalate and a gas, presumably cyclopropene. We found that the phthalate was indeed formed in quantitative yield. However, only 1% of cyclopropene was obtained, the rest being found in the form of a polymer. It might also be noted that the cleavage requires more vigorous conditions than does the

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[22] W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1951, p. 116.

[23] This experiment was performed by Dr. R. Ciula.

[24] This experiment was performed by Mr. D. Babcock.

[25] M. J. Schlatter, THIS JOURNAL, **63**, 1733 (1941); N. J. Demjanow and M. Dojarenki, *Ber.*, **56**, 2200 (1932).

[26] N. Collie and S. B. Schryver, *J. Chem. Soc.*, **57**, 767 (1890).

[27] J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

[28] W. R. Dunstan and E. Goulding, *J. Chem. Soc.*, **75**, 792, 1004 (1899).

[29] K. Alder and G. Jacobs, *Ber.*, **86**, 1528 (1953).

corresponding adduct with cycloöctatriene, which gives cyclobutene,[30] and this is in line with the greater destabilization due to bond angle deformation in cyclopropene.

In connection with the study of the microwave,[5] and infrared[3] spectra of cyclopropene, it was desired to obtain a deuterium-labeled sample. Since evidence has been obtained which indicates the vinyl hydrogen in a cyclopropene derivative to be moderately acidic,[31] the possibility of observing an exchange of hydrogen for deuterium during the formation of cyclopropene was examined.[32] Cyclopropyltrimethylammonium hydroxide was equilibrated with deuterium oxide and the resultant solution was pyrolyzed. The cyclopropene thus obtained contained 20% cyclopropene-$d_2$, 40% cyclopropene-$d_1$ and 40% cyclopropene-$d_0$. At least 80% of the deuterium was in the vinyl position, as indicated by an analysis of the n.m.r. spectrum of the dibromide. The facts that a considerable amount of dideuterated material was formed, and that most of the deuterium was in the vinyl position suggests that cyclopropene was the species which equilibrated and this may be evidence for enhanced acidity of the vinyl hydrogens. However, the exchange may involve the platinum catalyst.

## Experimental[33]

**Cyclopropene.**—Cyclopropene was prepared by a procedure little different than that of Schlatter[25] except that the conversion of cyclopropanecarboxylic acid to cyclopropylamine was effected using the Schmidt reaction. To a mixture of 500 ml. of C.P. chloroform (washed with sulfuric acid) and 100 ml. of concentrated sulfuric acid was added 43 g. (0.5 mole) of cyclopropanecarboxylic acid, followed by 36 g. of sodium azide added in small portions over the period of 1 hour with efficient stirring. The reaction mixture was heated to 50–55° for 5–8 hr. with stirring, or until the carbon dioxide evolution nearly ceased. The mixture was then added to ice and the chloroform layer was separated. The aqueous solution was treated with an excess of concentrated potassium hydroxide solution, and the amine was distilled into a small excess of 6 *N* hydrochloric acid. The acid solution was evaporated under reduced pressure to a small volume on a steam-bath, and finally dried over potassium hydroxide in a vacuum desiccator giving 28–35.5 g. (60–76%) of cyclopropylammonium chloride. The reaction could be conveniently carried out on a scale five times as large, the yield remaining essentially constant.

Cyclopropene was conveniently purified by vapor phase chromatography using a 9′ column (1″ i.d.) packed with 30% nitrobenzene on firebrick. The material thus obtained was free from the principal impurities: ethylene, carbon dioxide, methylacetylene and dimethyl ether.

When the cyclopropyltrimethylammonium hydroxide was equilibrated with deuterium oxide before pyrolysis, the cyclopropene obtained had 40% $d_2$, 40% $d_1$ and 20% $d_0$ as determined from the mass spectrum at an ionizing voltage sufficiently low to prevent cracking. The cyclopropene was converted to the dibromide, and the n.m.r. spectra of the dibromide and the unlabeled dibromide were compared. From both the ratio of the peak areas, and the appearance of the bands (deuterium giving no apparent spin–spin coupling), it was concluded that about 80% of the deuterium was in the vinyl position.

**Thermal Rearrangement.**—A mixture of cyclopropene and helium (1:5) was slowly swept with helium over the course of $^1/_6$ to $^1/_2$ hr. into a 12 × 300 mm. tube packed with glass helices and heated to either 325 or 425°. The effluent gas was passed through a liquid nitrogen cooled trap. The material in the trap was analyzed using the infrared spectrum. About a 50–80% recovery of gaseous material was obtained, longer contact times giving an apparently larger amount of polymerization in the heated tube. At 325° only a small amount of rearrangement was noted, but at 425° the product contained up to 80% methylacetylene, the conversion being dependent on the contact time. Attempts were not made to obtain a higher conversion because of the difficulty of controlling the flow at very high contact times. In a similar fashion, methylacetylene was passed through the tube, but the effluent gas did not contain a detectable amount of cyclopropene.

**Reaction with Cyclopentadiene.**—A mixture of cyclopropene and nitrogen was slowly passed into a solution of 3.5 g. of freshly distilled cyclopentadiene in 50 ml. of methylene chloride at 0°. The solvent was removed by distillation and the residue was purified by vapor phase chromatography using a silicone–Celite column and a temperature of 110°. There was obtained 5.4 g. (96% based on cyclopentadiene) of the adduct, m.p. 30–32°.

*Anal.* Calcd. for $C_8H_{10}$: C, 90.5; H, 9.5. Found: C, 90.4; H, 9.5.

The compound had an n.m.r. spectrum consisting of a triplet at 4.36, a multiplet at 7.22, a poorly resolved doublet at 8.26, a broad multiplet at 8.68, and a multiplet at 9.63. All of these were of equal area. The infrared spectrum had characteristic bands (those differentiating it from the *exo* isomer) at 9.54, 10.95 and 11.13 μ, whereas the *exo* isomer had characteristic bands at 6.28, 6.68, 9.22, 10.43 and 11.05μ.

**Reaction with Butadiene.**—A slow stream of cyclopropene mixed with nitrogen was passed into a solution of 3.2 g. of butadiene in 75 ml. of methylene chloride at room temperature. A Dry Ice–acetone-cooled condenser was used in order to minimize loss of butadiene and of cyclopropene. The reaction mixture was allowed to stand for 5 hours, and the solvent was then removed by distillation. The residue was purified by gas chromatography giving 2.0 g. (37%) of the adduct, b.p. 106–109° (micro b.p.), $n^{25}$D 1.4749.

*Anal.* Calcd. for $C_7H_{10}$: C, 89.3; H, 10.7. Found: C, 89.1; H, 10.6.

The adduct absorbed one mole of hydrogen over a platinum catalyst. The product was found to be norcarane by a comparison infrared and n.m.r. with an authentic sample prepared by the procedure of Simmons and Smith.[12] The n.m.r. spectrum had bands at 4.50, 7.65, 9.03 (broad) and 9.60–9.69. The band at 7.65 had approximately twice the area of the other bands.

***trans*-Dibromocyclopropane.**—A stream of cyclopropene in nitrogen was passed into a solution of bromine in carbon tetrachloride at 0° until the bromine color had been discharged. Distillation gave 57% (based on the bromine used) of the dibromide having b.p. 40–50° at 27 mm., $n^{25}$D 1.5301. The n.m.r. spectrum had two triplets, one at 6.90 and the other at 8.53. The coupling constant was 6.5 cycles.

**Diiodocyclopropane.**—Cyclopropene was added to a solution of iodine in carbon tetrachloride at room temperature. Distillation of the solution gave 64% (based on iodine) of the diiodide, b.p. 45–47° at 1 mm., $n^{25}$D 1.6738.

*Anal.* Calcd. for $C_3H_4I_2$: C, 12.3; H, 1.4; I, 86.4. Found: C, 13.3, 12.9; H, 1.5, 1.5; I, 85.3, 85.5.

The n.m.r. spectrum had a triplet at 8.65 and at 7.27, which probably correspond to those of the *trans*-diiodide. There were also two weaker triplets at 8.12 and 9.16 which may be due to the methylene group of the *cis*-diiodide, and one at 7.38 which may be due to the vinyl hydrogens of the *cis*-compound.

***cis*-Dideuteriocyclopropane.**—A Grignard reagent was prepared from 5 g. of 1,2-dibromocyclopropane, 1.22 g. of magnesium and 20 ml. of anhydrous ether. The formation of the Grignard reagent was exothermic, but still about 40% of the magnesium failed to react even after heating the solution for 3 hours. To the solution was added dropwise 2 ml. of deuterium oxide, and the cyclopropane formed was swept into a liquid nitrogen-cooled trap. The cyclopropane was purified by vapor phase chromatography giving a 10% yield of material having 86% $d_2$, 8% $d_1$ and 6% $d_0$ (determined mass spectrometrically). The infrared spectrum was

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(30) A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, THIS JOURNAL, **74**, 4867 (1952).

(31) K. B. Wiberg, R. K. Barnes and J. Albin, *ibid.*, **79**, 4994 (1957).

(32) This experiment was performed by Dr. J. Albin.

(33) The n.m.r. spectra were obtained using a Varian spectrometer operating at 60 mc. The band positions are reported on the τ scale.[8]

compared with that of an authentic sample of *cis*-cyclopropane-$d_2$ prepared by the catalytic hydrogenation of cyclopropene.[18] The *cis* and *trans* isomers are easily differentiated by the fact that the *trans* isomer has a strong band at 12.77$\mu$ whereas the *cis* isomer has no band at this position. No cyclopropene was formed in the reaction giving the Grignard reagent.

***cis*-Cyclopropanedicarboxylic Acid.**—The Grignard reagent was prepared as described above using 11 g. of 1,2-dibromocyclopropane and 2.9 g. of magnesium in 40 ml. of ether. The solution was cooled in a Dry Ice–acetone-bath and dry carbon dioxide was added with stirring. After the reaction appeared complete, the reaction mixture was hydrolyzed with 25% sulfuric acid. The aqueous layer was saturated with sodium chloride, and extracted with ether. The combined ether solutions were evaporated giving a viscous oil which could not be induced to crystallize. The acid was converted to the ethyl ester by heating for 3 hours with 50 ml. of absolute ethanol and a few drops of concentrated hydrochloric acid. The solvent was removed by distillation and the residue was taken up in ether. The latter solution was extracted with 10% potassium carbonate solution, the solution was dried and the ether was removed by distillation. The residue (10% based on dibromocyclopropane) was found to have infrared and n.m.r. spectra identical with that of authentic diethyl *cis*-cyclopropane-1,2-dicarboxylate prepared by the esterification of the anhydride of *cis*-cyclopropane-1,2-dicarboxylic acid.

**Argentic Complex.**—Purified cyclopropene was passed into a 30% aqueous solution of silver nitrate. The cyclopropene was quantitatively absorbed, and after about a minute a black precipitate formed. In another experiment, cyclopropene was bubbled into ammoniacal silver nitrate solution. Again, complete absorption occurred, and a black precipitate was formed almost immediately. The black precipitates were found to be for the most part soluble in 30% perchloric acid solution, whereas silver (as formed in a Tollens test) is not. A yellow-white gum was formed in the reaction. This was found to be insoluble in all common solvents.

**Reaction with Diphenyldiazomethane.**—To a solution of diphenyldiazomethane prepared from 2.5 g. of benzophenone hydrazone in 50 ml. of methylene chloride was added 0.5 g. of finely divided copper powder. The solution was cooled in liquid nitrogen and approximately 1 g. of cyclopropene was distilled into the reaction flask. The solution was kept in a Dry Ice–acetone-cooled bath for 1.5 hours with occasional shaking, and it was then allowed to warm to room temperature. During this time the color lightened to yellow. The solution was decanted from the copper powder and evaporated to a small volume under reduced pressure. The remaining oil was taken up in hot 95% ethanol, the solution was filtered and then cooled giving 1 g. of material, m.p. 119–121°, in the form of yellow-tan needles.

*Anal.* Calcd. for $C_{16}H_{14}N_2$: C, 81.1; H, 6.4. Found: C, 81.7; H, 6.1.

Oxidation with basic permanganate gave benzophenone, identified as the 2,4-dinitrophenylhydrazone, m.p. 235–237°, mixed m.p. with an authentic sample, 235–237.5°.

**Reaction with Ethyl Diazoacetate.**—To a solution of 3.0 ml. of ethyl diazoacetate in 10 ml. of methylene chloride which was cooled in liquid nitrogen was added 1.5 ml. of cyclopropene. The reaction mixture was placed in a Dry Ice–acetone-bath and then allowed to warm to room temperature. At about −40°, an exothermic reaction occurred. Distillation gave 1.5 g. of material, b.p. 90–100° at 0.4 mm., and some higher boiling material.

*Anal.* Calcd. for $C_7H_{10}O_2N_2$: C, 54.5; H, 6.5. Found: C, 54.5; H, 6.4.

**Pyrolysis of Cyclopropyldimethylamine Oxide.**—To an ice-cooled solution of 25 ml. of 30% hydrogen peroxide in 50 ml. of water was added 8.5 g. of cyclopropyldimethylamine with stirring and cooling, at such a rate as to keep the temperature below 10°. The mixture was allowed to warm to room temperature, a slight exothermic reaction being noted. The mixture was stirred overnight. The excess hydrogen peroxide was then decomposed with a small amount of platinized asbestos and the solution was concentrated under reduced pressure to about 15 ml.

The solution was pyrolyzed at 320° using the apparatus employed for the pyrolysis of the quaternary ammonium hydroxide. The products of the reaction were swept with nitrogen through a trap containing 10% hydrochloric acid and then through a drying tower (calcium sulfate) and a liquid nitrogen cooled trap. The hydrochloric acid solution was made basic with potassium hydroxide, and the amine was isolated in the usual way. There was obtained 2.0 g. of material, b.p. 58°, whose infrared spectrum was found to be identical with cyclopropyldimethylamine. No cyclopropylmethylamine was found. The liquid nitrogen-cooled trap was found to contain no cyclopropene. The reaction was also carried out using platinized asbestos as a catalyst, as in the Hofmann degradation, but again no cyclopropene was formed.

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[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY,[1] BIOLOGY DIVISION, OAK RIDGE, TENN.]

# Characterizations and Some Chemical Reactions of Periodate-oxidized Nucleosides[2]

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Phenylhydrazine reacts with the periodate oxidation products of adenosine, guanosine, uridine and cytidine to form bisphenylhydrazones, which have been isolated and characterized. These substances react further with phenylhydrazine to form adenine, guanine, uracil, and cytosine and 2- and 3-carbon fragments. Sodium borohydride reduces both aldehyde groups of the oxidized nucleosides when the reaction is carried out under alkaline conditions, but selective reduction of the aldehyde group distal to the purine or pyrimidine ring occurs under slightly acidic conditions. Ion exchange and paper chromatographic methods have been developed for the examination of the dialdehydes and the corresponding reduction products obtained from them. Evidence is presented indicating that the acid hydrolysis of the completely reduced products, the tri-alcohols, is probably initiated at the glycosidic linkage. A new micro method for measuring and removing periodate and iodate essentially in one step has been developed.

## Introduction

Studies on the oxidation of sugar glycosides by periodate to yield dialdehydes have played an important role in the determination of carbohydrate configurations as first shown by Jackson and Hudson[3] and later extended by Smith and Van Cleve.[4] The reaction as applied to the nucleosides[5] distinguishes between deoxy- and ribonucleosides[6]

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[1] Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

[2] Parts of this communication were presented to the American Chemical Society, Atlantic City, N. J., September, 1959, and at Cleveland, Ohio, April, 1960.

[3] E. Jackson and C. S. Hudson, THIS JOURNAL, **59**, 944 (1937).

[4] F. Smith and J. W. Van Cleve, *ibid.*, **77**, 3091 (1955).

[5] (a) J. Baddiley in "The Nucleic Acids," Vol. 1, eds., E. Chargaff and J. N. Davidson, Academic Press, Inc., New York, N. Y., 1955, p. 147; (b) G. R. Barker, *Advances Carbohydrate Chem.*, **11**, 285 (1956).

[6] D. M. Brown and B. Lythgoe, *J. Chem. Soc.*, 1990 (1950).