**Cleavage of the Pinacolone: 1,1-Dianisylethane.**—The pinacolone, 1.5 g., was heated for thirty minutes with 20 g. of potassium hydroxide at 170–180°. The cooled melt was dissolved in 100 cc. of water and the insoluble material collected on a filter. This was recrystallized three times from ethyl alcohol, appearing as fine, white platelets, m. p. 70–72°. A 50–50 mixture of this compound with the original ketone melted around 60°.

*Anal.* Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.47; H, 7.80.

**Beckmann Rearrangement: 1,1-Dianisylethene.**—A suspension of 0.77 g. of 3,3-dianisyl-2-butanone oxime and 0.2 g. of phosphorus pentachloride in 30 cc. of pure, dry ether was shaken for twenty minutes, or until the oxime had dissolved. When the solution was allowed to stand overnight in the cold it deposited large, clear hexagonal plates. Evaporation and recrystallization yielded 0.47 g. of 1,1-**dianisylethene**, m. p. 141–143°.[11]

*Anal.* Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.06; H, 6.16.

## Summary

Electrolytic reduction of *p*-methoxyacetophenone has been found to produce a mixture of the two possible diastereoisomeric pinacols in excellent yield. These pinacols have been characterized but attempted dehydration to the butadiene has led only to the pinacolone, 3,3-dianisyl-2-butanone.

URBANA, ILLINOIS RECEIVED DECEMBER 22, 1943

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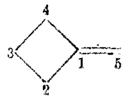
[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 950]

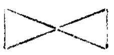
# The Structures of Methylenecyclobutane and of 1-Methylcyclobutene

BY W. SHAND, JR., VERNER SCHOMAKER AND J. RODNEY FISCHER

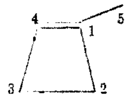
The hydrocarbon prepared by Gustavson[1] by the action of zinc dust on pentaerythrite tetrabromide has been subjected to an intensive chemical investigation[2] on the basis of which structure (I) has been assigned to this substance. The structure may be regarded as definitely established in spite of the appearance of a recent article by Rogowski,[3] who advocated the spiropentane[3a] structure (II) on the basis of electron diffraction studies. A more recent electron diffraction investigation by Bauer and Beach[4] with results in essentially complete disagreement with those of Rogowski is compatible with structure (I) and eliminates structure (II). The hydrocarbon (III) was also first obtained by Gustavson.[5] It is not as readily accessible as (I) and consequently has received less attention from chemists; its structure, however, is not in doubt.[2]



(I)



(II)



(III)

The present investigation was undertaken with the aim of isolating methylenecyclobutane and 1-methylcyclobutene in a state as pure as possible and verifying their structures by the electron diffraction method. It was found, however, that the two compounds cannot readily be distinguished from each other by electron diffraction studies alone, and a determination of only some of the structural details was made, the others being assumed to correspond to the chemically established identity of each compound. The preparation and physical constants of methylenecyclobutane and 1-methylcyclobutene are accordingly described in some detail.

**Preparation of Methylenecyclobutane.**[6]—Crude pentaerythrityl bromide was made by the procedure in "Organic Syntheses.[7]" Five moles of pentaerythrytol was converted in a single operation to tetrabromide which was washed with water and 95% ethanol[7] and air-dried, average yield 88%. The apparatus used for the hydrocarbon preparation consisted of a 12-liter flask fitted with a three-neck adapter carrying a dropping funnel, mercury-sealed stirrer, and a 38-cm. column without packing equipped with a cold finger at the top and connected to an ice-water cooled condenser; the receiver was surrounded with ice. An intimate mixture of 776 g. (2 moles) of crude tetrabromide and 785 g. (12 moles) of zinc dust was placed in the flask and one liter of water *cautiously* added. The mixture was heated to 85° on a water-bath and 500 cc. of ethanol was added portionwise (*cf.* Philipow, *loc. cit.*) with stirring over a period of two hours or until no more hydrocarbon distilled; frothing was controlled by raising or lowering the stirrer. At the end of the reaction the bath temperature was raised to 95°, forcing over the last traces of hydrocarbon together with some alcohol. The distillate was washed with two 100-cc. portions of water and dried over calcium chloride at 0°, yield 115 g. In a series of runs the yield varied between 70 and 90%. A quantity of the crude hydrocarbon (1340 g.) was twice fractionated through a 22-mm. inside diameter column, 6.5 ft. long, packed with glass helices and fitted with a total reflux, variable take-off

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(1) Gustavson, *J. prakt. Chem.*, [2] **54**, 97 (1896).

(2) More pertinent references: Demjanow, *Ber.*, **41**, 915 (1908); Faworsky and Batalin, *ibid.*, **47**, 1648 (1914); Philipow, *J. prakt. Chem.*, [2] **93**, 162 (1916); Demjanow and Dojarenko, *Ber.*, **55**, 2718, 2727 (1922). The last paper cited demonstrates the identity of the Gustavson hydrocarbon with methylenecyclobutane independently synthesized by a method indicative of structure.

(3) Rogowski, *Ber.*, **72**, 2021 (1939). Structure (II) had previously been advanced in the earlier part of the chemical investigation, but the facts cited in its favor proved on closer examination to be without foundation: Fecht, *Ber.*, **40**, 3883 (1907), *cf.* Mereschkowski, *J. Russ. Phys.-Chem. Soc.*, **46**, 517 (1914) [*Chem. Abst.*, **8**, 3187 (1914); *Chem. Zentr.*, **85**, II, 1266 (1914)]; Zelinsky, *Ber.*, **46**, 160 (1913), *cf.* Philipow, *loc. cit.*, Ingold, *J. Chem. Soc.*, **123**, 1706 (1923).

(3a) A third $C_5H_8$ hydrocarbon from pentaerythrityl bromide, not identical with either of the Gustavson hydrocarbons discussed in this paper, was recently reported by M. J. Murray and E. H. Stevenson and assigned to formula (II); THIS JOURNAL, **66**, 314 (1944).

(4) S. H. Bauer and J. Y. Beach, THIS JOURNAL, **64**, 1142 (1942).

(5) Gustavson, *J. prakt. Chem.*, [2] **54**, 104 (1896).

(6) The preparations described here were carried out by J. R. F. For details see his Masters' Thesis, California Institute of Technology, 1941.

(7) Schurink in "Organic Syntheses," Vol. **17**, p. 73, J. Wiley, and Sons, Inc., New York, N. Y., 1937.

head. About 80% of the distillate[8] boiled at 41.0–41.7° at 750 mm.; this material was refractionated a third time through a 3-foot column packed with helices and a middle portion reserved for electron diffraction study, b. p. 41.39° at 750 mm., $n^{10}$D 1.4266, $n^{15}$D 1.4236, $n^{20}$D 1.4210, $d^{20}_4$ 0.7401, $d^{25}_4$ 0.7349. The product obtained by Whitmore and Williams and used by Bauer and Beach, and identified as methylenecyclobutane by ozonolysis had the constants b. p. 41.3° at 746 mm., $n^{20}$D 1.4203–6.

**Preparation of 1-Methylcyclobutene.**—Although Philipow[2] claimed to have fractionated this hydrocarbon from the mixture obtained on treating pentaerythrite tetrabromide with zinc dust, the presence of a constant boiling fraction in this range could not be detected.[9] Several unsuccessful attempts were made to prepare methylcyclobutene by isomerization of methylenecyclobutane over an alumina catalyst at 300°. The greater part of the hydrocarbon was converted to lower boiling material but apparently this consisted almost entirely of products of ring-splitting.[10] Attempts to dehydrate 1-methylcyclobutanol[5,4,11] were also unsuccessful; the use of 60% sulfuric acid and of anhydrous oxalic acid gave polymers while the tertiary alcohol was recovered unchanged after refluxing with iodine.

1-Chloro-1-methylcyclobutane was prepared in 80% yield by treating methylenecyclobutane with excess concentrated aqueous hydrochloric acid at 0°. After shaking for one hour, the lighter phase was washed with sodium carbonate solution, dried over calcium chloride and distilled, b. p. 90–91° at 745 mm., $n^{20}$D 1.4311, $n^{25}$D 1.4288, $d^{20}_4$ 0.9495, $d^{25}_4$ 0.9444. The corresponding bromide was prepared in 72% yield from methylenecyclobutane and 62% aqueous hydrogen bromide at 0°, mixing by hand at first and then shaking mechanically for one hour. The bromide layer was worked up in the above manner, b. p. 55–57° at 100 mm., $n^{20}$D 1.4698, $n^{25}$D 1.4673, $d^{20}_4$ 1.3179, $d^{25}_4$ 1.3110. 1-Iodo-1-methylcyclobutane was prepared by shaking 68 g. (1 mole) of methylenecyclobutane in a glass-stoppered bottle with a solution of 154 g. (1.2 moles) of hydrogen iodide in 200 g. of glacial acetic acid at 0°.[6] The reaction mixture was poured into one liter of water, the heavy phase separated and washed with bisulfite and carbonate solutions and finally with water, crude yield 94%. At 20 mm. the product boiled at 40–42°, $n^{25}$D 1.5215, $d^{20}_4$ 1.604, yield 76%.

The chloride, bromide, and iodide were added dropwise under identical conditions to a 100% excess of a boiling solution of potassium hydroxide dissolved in cellosolve (ethylene glycol monoethyl ether). The mixed hydrocarbons produced were collected (yields from chloride 40%, bromide 60%, iodide 60%) and roughly analyzed by comparison[6] of densities and refractive indices with the values found for the pure hydrocarbons. The material obtained from the chloride and from the bromide contained methylenecyclobutane and 1-methylcyclobutene in a ratio of about 2:1, while in the case of the mixture obtained from the iodide, the reverse ratio obtained.

A modification of the original method of Gustavson[5] was therefore employed for the preparation of 1-methylcyclobutene in quantity. Fifty-six grams (1 mole) of potassium hydroxide was dissolved in 250 cc. of cellosolve (cellosolve gave higher yields than ethanol or ethanol–water) and this solution heated to boiling in a 500-cc. flask fitted with dropping funnel and reflux condenser through which water at 45° was circulated. The outlet at the top of the condenser led to another condenser set for downward distillation which was cooled by ice-water and then into a receiver cooled in a dry-ice bath. Ninety-eight grams (0.5 mole) of crude tertiary iodide was added dropwise over a period of two hours to the refluxing alkali solution and the hydrocarbon product washed with ice-water and dried over magnesium perchlorate, yield 20.4 g.

The crude hydrocarbon mixture (233 g.) from several of the above experiments was fractionated twice through the 6.5 ft. column described previously, using, because of the small amount of material available, a higher boiling hydrocarbon still-base. A third fractionation was carried out using a spinning band column similar to the one described by Baker, *et al.*[12] This column had the equivalent of 18 theoretical plates at the reflux rate and throughput used. The considerable portion of material which boiled at 37–38° at 748 mm. in this third fractionation was fractionated again with the spinning band column to obtain material of constant refractive index, b. p. 37.1° at 750 mm., $n^{18}$D 1.4088, $d^{20}_4$ 0.7244, $d^{25}_4$ 0.7188. This material was used for the electron diffraction investigation.

## Electron Diffraction Investigation

**Experimental.**—The electron diffraction apparatus used in this investigation has been described by Brockway.[13] The camera distance was 10.89 cm., and the wave length of the electrons, determined from transmission photographs of gold foil, was 0.0615 Å. The photographs, made with the samples at about 25°, showed eight maxima and minima extending to $s_0$ values of about twenty-nine.

**Interpretation.**—Both the radial distribution method[14] and the correlation method[15] were used in interpreting the electron diffraction photographs. The radial distribution curves were calculated according to the formula where $I(s_k)$

$$rD(r) = \sum_k I(s_k)e^{-as_k^2} \sin s_k r$$

is a visually estimated intensity assuming no falling off of intensity with $s_k$, and $a$ is chosen so that $e^{-as^2_{\max.}} = 0.10$. A plot of the visually estimated intensities was divided into about 50 segments, and the $I(s_k)$'s taken at each endpoint.[16]

Theoretical intensity curves were calculated using the simplified theoretical scattering formula

$$I(s) = \sum_i \sum_j Z_i Z_j \frac{\sin r_{ij}s}{r_{ij}} e^{-a_{ij}s^2}$$

The constant $a_{ij}$ in the exponential temperature factor term was given the value 0.002 for bonded C—H terms, 0.004 for non-bonded C—H terms, and 0.0 for all C—C terms. The contribution of C—H terms is important out to about $s = 20$.

**Methylenecyclobutane.**—The radial distribution curve shown at the top of Fig. 1 can be interpreted on the basis of a model with structure (I). Peaks occur at 1.09 Å., corresponding to the C—H bond, 1.55 Å., the C—C single-bond distance, 2.20 Å., the cross-ring distance, and 2.61 Å.,

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(8) Regarding the composition of the forerun see footnote (5) of reference (4).

(9) Investigators other than Philipow obtained methylcyclobutene by the original Gustavson method, *cf.* for example Dojarenko, ref. (10).

(10) Compare Dojarenko, *Ber.*, **59**, 2933 (1926).

(11) Demjanow and Dojarenko, *J. Russ. Phys.-Chem. Soc.*, **45**, 176 (1913) [*Chem. Abst.*, **7**, 2226 (1913); *Chem. Zentr.*, **84**, I, 2027 (1913)]. The observed constants were b. p. 115–118° at 747 mm., $n^{24}$D 1.4333, $d^{23}_4$ 0.8971, m. p. −6 to −3°, solubility 1 part in 6.5–7 parts water at 25°, phenylurethan m. p. 139.9° (cor.) from isopropyl ether.

(12) Baker, Barkenbus and Roswell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 468 (1940).

(13) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(14) L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

(15) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(16) R. A. Spurr and V. Schomaker, THIS JOURNAL, **64**, 2693 1942).

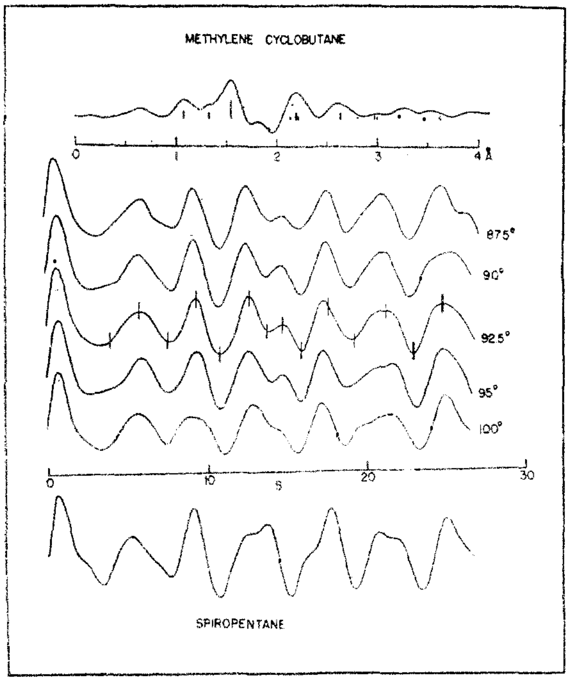

Fig. 1.

the distance between the side-chain carbon and the non-bonded adjacent ring carbon atom. The double-bond distance is not resolved, although a small inflection occurs at 1.33 Å. The spiropentane structure (II) as reported by Rogowski[3] can be ruled out, since it would give only two main peaks, at about 1.54 and 2.87 Å. Other structures differing widely from (I) with respect to their interatomic distances can likewise be ruled out by comparison with the radial distribution function. The chemical identification was accordingly accepted, and theoretical intensity curves calculated for structure (I).

Certain simplifying assumptions were made to reduce the number of structural parameters. The C—H bond distances were taken to be 1.09 Å., and the H—C—H angle on the ring to be 116°. The plane of these H—C—H's was perpendicular to the ring plane and bisecting the ring angles. Moreover, the carbon atoms were assumed to be coplanar and the C—C single-bond distances were taken as being all alike, reducing the problem to one of three parameters, namely, the C—C single-bond distance, the C—C double-bond distance, and an angle of the ring. The single-bond distance was taken from the radial distribution curve to be 1.55 Å., while the double-bond distance and the $\angle$ $C_4C_1C_2$ were varied in calculating the theoretical intensity curves. Curves calculated for values of $\angle$ $C_4C_1C_2$ varying from 87.5° to 100° with a double-bond distance of 1.34 Å. are shown in Fig. 1. The characteristic features of the observed pattern are the roundedness of the first maximum, the shelf-like appearance of the fourth maximum, the roundedness and almost complementary asymmetry of the sixth and seventh maxima. The eighth maximum (not shown) was a sharp peak whose position varied little from curve to curve. Best agreement is given by the curve marked 92.5°. The non-bonded C···C distances in this model are 2.14, 2.24, 2.65 and 3.48 Å.; most of the important C···H distances fall at about 2.20 Å. These distances and their relative weights are shown with the radial distribution curve in Fig. 1. Curves calculated with double bond distances of 1.30 and 1.38 Å. do not give as good agreement with the observed pattern. In general the second minimum is raised, the sixth maximum becomes more symmetrical, and the seventh maximum asymmetrical on the inner side instead of the outer side. Best agreement for these curves is found for $\angle$ $C_4C_1C_2$ = 90° and C=C = 1.30Å. This is to be expected since for these values of the parameters the distances $C_5 \cdots C_2$, $C_5 \cdots C_4$, and $C_5 \cdots C_3$ are the same as for the 92.5° model with C=C = 1.34 Å. The main difference arises in the cross-ring distances, which are different in the 92.5° model, and alike in the square model.

The effect of removing the restrictions that the ring be coplanar, and that the C—C single-bond distances be all alike was investigated, these variations being made separately. Curves were calculated in which the $C_5$, $C_1$, $C_2$ and $C_4$ atoms were coplanar (as in ethylene), and the $C_3$ atom moved perpendicular to this plane. Curves were also calculated for coplanar models with C—C single-bond distances adjacent to the double bond different from those opposite the double bond. Although these theoretical curves showed small but definite points of disagreement with the observed pattern, especially at the second minimum and the sixth and seventh maxima, it became evident that with the available data the complete correlation procedure with the admission of these additional variations could not be made to give more precise information than was already available from the radial distribution function. The final parameter determination was accordingly carried out with the assumptions mentioned in the preceding paragraph.

Quantitative comparison (Table I) of the observed and calculated $s$ values $\left(s = \frac{4\pi}{\lambda} \sin \theta/2\right)$ also shows that the best agreement is for the 92.5° model with C—C single-bond distance 1.55 Å. and C—C double-bond distance 1.34 Å. The 90° model with C—C single-bond distance 1.55 Å. and C—C double-bond distance 1.30 Å. shows a larger average deviation. As discussed above this curve is also considered less satisfactory on the basis of qualitative agreement with the appearance of the observed pattern. The final results are C—C = 1.55 ± 0.02 Å., C=C = 1.34 ± 0.03 Å., and $\angle$ $C_4C_1C_2$ = 92.5° ± 2°, in fair agreement with Bauer and Beach, who reported C—C = 1.56 ± 0.03 Å., C=C = 1.34 ± 0.02 A., and $\angle$ $C_4C_1C_2$ = 90°.

In spite of the exclusion of the spiropentane model by the radial distribution curve, a theoretical intensity curve shown in Fig. 1 was calculated for the spiropentane model of Rogowski[3] for the full $s_0$ range of our pictures. This curve is in essentially complete disagreement with the observed diffraction pattern, although the positions of the main features are similar.[4]

**1-Methylcyclobutene.**—The appearance of the diffraction pattern is generally similar to that observed for methylenecyclobutane, but shows numerous distinct points of difference. For 1-methylcyclobutene the first maximum is broader, and higher on the inner side; the shelf-like fourth maximum is less distinctly separated from the third; the fifth minimum is broader and the fifth maximum rises more gradually on the inner side. The sixth maximum is stronger and sharper, and the seventh maximum shows structure on the outer side, which is not too clearly distinguishable. The stronger peaks of the radial distribution curve marked RD in Fig. 2 are at 1.09, 1.54, 2.16 and 2.72 Å. The double-bond distance is not resolved. It was varied from 1.30 to 1.38 Å. in calculating the theoretical intensity curves.

Since the double bond is in the ring in 1-methylcyclobutene there is no doubt that the carbon atoms are coplanar. The same assumptions regarding the hydrogen atoms were made as above. The C—C single-bond distance was taken from the radial distribution curve to be 1.54 Å. The angle $C_5C_1C_2$ was varied from 110 to 140°. About 25 theoretical curves were calculated, of which representative examples are shown in Fig. 2. Curves A to G have double-bond distance 1.34 Å. and the $\angle C_5C_1C_2$ indicated; curves H and I have double-bond distances 1.30 and 1.38 Å., respectively, with $\angle C_5C_1C_2 = 125°$. In all except curves F and G the ring structure was made symmetrical ($\angle C_2C_3C_4 = \angle C_1C_2C_3$; $\angle C_3C_4C_1 = \angle C_4C_1C_2$). For curve F the ring was distorted by increasing the $\angle C_4C_1C_2$ by 5°, and in curve G by decreasing the same angle 5°, changes in other angles being made symmetrically but retaining the same external $\angle C_5C_1C_2$ ( = 125° in these curves). On the basis of the features of the observed pattern described above, best agreement was found for the symmetrical ring with double-bond distance 1.34 Å. and 120° < angle $C_5C_1C_2$ < 130°.[17] Curve C (125°) was chosen as best, with calculated non-bonded $C \cdots C$ distances 2.11, 2.71, 2.74 and 3.63 Å. The most important $C \cdots H$ terms are in the neighborhood of 2.20 Å. These distances with their relative weights are shown on the curve RD of Fig. 2. Quantitative comparison of observed and calculated $s$ values for Curve C (125°) is made in Table II. Our final results are C—C = 1.54 ± 0.03 Å., C=C = 1.34 ± 0.03 Å., $\angle C_5C_1C_2 = 125° \pm 4°$, $\angle C_4C_1C_2 = 93°40' \pm 3°$, etc. (*i. e.*, symmetrical ring structure ±3° distortion).

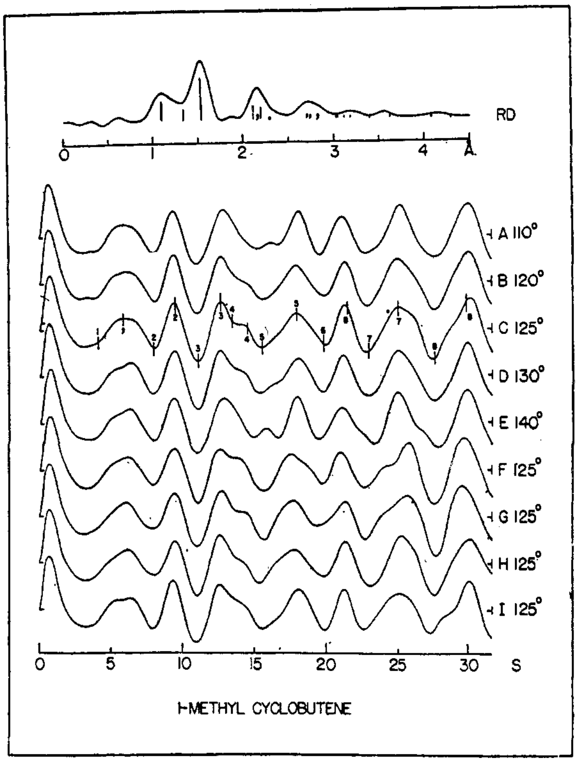

Fig. 2.

TABLE I

METHYLENECYCLOBUTANE

| Max. | Min. | $s_o$ | $s_c$ (92.5°) 1.34 | $s_o/s_c$ | $s_c$ (90°) 1.30 | $s_o/s_c$ |
|---|---|---|---|---|---|---|
| | 1 | 4.14 | 3.61 | (0.872) | 2.82 | (0.688) |
| 1 | | 5.89 | 5.90 | (1.000) | 6.06 | (1.030) |
| | 2 | 7.42 | 7.78 | 1.048 | 7.92 | 1.067 |
| 2 | | 9.44 | 9.35 | 0.990 | 9.27 | 0.982 |
| | 3 | 10.84 | 11.00 | 1.014 | 10.81 | 1.017 |
| 3 | | 12.66 | 12.66 | 1.000 | 12.63 | 0.998 |
| | 4 | 13.80 | 14.04 | 1.017 | 13.95 | 1.011 |
| 4 | | 14.76 | 14.83 | 1.004 | 14.89 | 1.009 |
| | 5 | 16.18 | 16.05 | 0.992 | 16.02 | 0.990 |
| 5 | | 17.70 | 17.36 | .980 | 17.47 | .987 |
| | 6 | 19.36 | 19.10 | .987 | 19.07 | .985 |
| 6 | | 21.32 | 21.33 | 1.000 | 20.67 | .969 |
| | 7 | 23.05 | 23.03 | 0.999 | 22.70 | .984 |
| 7 | | 24.93 | 24.91 | .999 | 25.37 | 1.017 |
| 8 | | 29.30 | 29.31 | 1.000 | 29.30 | 1.000 |
| | | | | 1.002 ± 0.011 | | 1.002 ± 0.019 |

**Discussion.**—Although the diffraction data for the two substances considered here can be interpreted satisfactorily on the basis of planar cyclic models in agreement with the chemical identification of these substances as methylene-

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[17] The $C_5 \cdots C_2$ and $C_5 \cdots C_3$ distances and their associated $C \cdots H$ terms, which together are the most important in determining the structure-sensitive features of the theoretical curves, are equal at about $\angle C_5C_1C_2 = 125°$. Consequently a considerable variation of this angle in either direction produces only relatively small differences in the resulting curves, and prevents a close determination of the angle. Similarly curves calculated for distortions of 2 and 5° of the ring in either direction in the manner described above show that distortion of about 5° in either direction is required to produce definite disagreement for the best curve, and does not improve agreement for the other curves.

TABLE II

1-METHYLCYCLOBUTENE

| Max. | Min. | $s_0$ | $s_c$ | $s_0/s_c$ |
|---|---|---|---|---|
| | 1 | 4.09 | 3.30 | (0.807) |
| 1 | | 5.81 | 5.97 | (1.027) |
| | 2 | 7.89 | 8.01 | 1.014 |
| 2 | | 9.43 | 9.38 | 0.995 |
| | 3 | 11.00 | 11.00 | 1.000 |
| 3 | | 12.57 | 12.57 | 1.000 |
| | 4 | 13.39 | 13.57 | 1.013 |
| 4 | | 14.46 | 14.29 | 0.989 |
| | 5 | 15.51 | 15.47 | .998 |
| 5 | | 17.89 | 17.84 | .998 |
| | 6 | 19.78 | 19.95 | 1.008 |
| 6 | | 21.49 | 21.21 | 0.987 |
| | 7 | 22.97 | 22.70 | .989 |
| 7 | | 24.95 | 24.91 | .998 |
| | 8 | 27.51 | 27.39 | .996 |
| 8 | | 29.52 | 29.85 | 1.009 |
| | | | | 0.999 ± 0.006 |

cyclobutane and 1-methylcyclobutene, it is clear from the similarity of the photographs that a unique identification by means of electron diffraction alone would be difficult, and, from a comparison of the theoretical curves, impossible. This is shown by the practical identity of curve 92.5° of Fig. 1, the best methylenecyclobutane curve, with the 1-methylcyclobutene curves B (120°) and C (125°) of Fig. 2.[18] This is to be expected for molecules whose scattering distances ($r_{ij}$'s) differ only in what amounts to second order effects: about 70% of the scattering (based on the weight of the coefficients $Z_iZ_j/r_{ij}$) is due to $r_{ij}$'s identical for the two models and the remainder is due to $r_{ij}$'s which are not markedly different. It should be emphasized again that the attempt to differentiate between different chemical structures by the electron diffraction method may not always lead to a unique result, especially when a reasonably great variation of the models representing the various chemical structures is allowed. Where the proposed structures are, however, fundamentally different in geometrical design, the corresponding sets of interatomic distances are usually quite different and a definite choice is made possible.[19] Thus the comparison of the theoretical curves and the diffraction photographs provides definite detailed evidence that neither of our substances is spiropentane.

Moreover, a preliminary comparison of the radial distribution curves with the distances to be expected for the models in question at once makes improbable all of the other isomers which contain no four-membered ring, mainly because none of these would give a strong peak at about 2.2 Å. but only a C···H peak, while suggesting the possibility that for 3-methylcyclobutene a reasonable model leading to intensity curves in agreement with the photographs (especially of 1-methylcyclobutene) could be found. It was not thought profitable, however, further to consider these various structures inasmuch as there seemed to be no doubt about the chemical identification and it seemed likely that even after careful consideration by the correlation procedure not all of them could be ruled out with certainty.

The question of the distribution of "strain" in these molecules is of interest. In methylenecyclobutane the strain in the four-membered ring can be taken up by expanding the H—C—H angle to compensate for the compression of the C—C—C angle at the $C_2$, $C_3$ and $C_4$ positions; at $C_1$ such compensation cannot occur except by increase of the angle $C_4C_1C_2$, as observed. In 1-methylcyclobutene a symmetrical ring structure would be expected if the $C_5C_1$ single bond were sterically equivalent to the C—H single bond. The angle $C_5C_1C_2$ which distributes equally the distortions from the normal values of the bond angles about the $C_1$ carbon atom is 125°, in agreement with the angle 125 ± 4° found above. The angle distortion for the system C—C—C is then nearly equal to that for C═C—C, indicating that in this case at least the effective bending constants for the two systems are apparently not markedly different.

The results of Rogowski[3] are not clarified. A radial distribution analysis of his $s_0$ values leads to the distances 1.55 and 2.88 Å., in agreement with the spiropentane model. In the absence of more details on the preparation and physical constants of the substance used in his investigation no further explanation can be given than was offered by Bauer and Beach.

The authors wish to express their thanks to Dr. E. R. Buchman for suggesting this research, and for his assistance and interest in the work.

## Summary

The preparation and physical constants of methylenecyclobutane and 1-methylcyclobutene are described. The electron diffraction investigation of these compounds shows that they are cyclic structures with the expected configurations and distances.

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[18] The similarity of the theoretical curves was overlooked by Bauer and Beach[4] because an error in the cross-ring distance was made in the calculation of their curves E for 1-methylcyclobutene and F for 3-methylcyclobutene. Their model E (private communication from Professor Bauer) was nearly the same as our D (130°).

[19] See for example R. A. Spurr and V. Schomaker, *loc. cit.*; J. Waser and V. Schomaker, THIS JOURNAL, 65, 1451 (1943).