No secondary alcohol was detected; the larger part of the liquid began to decompose and carbonize at a bath temperature of 180° and pressure of 4 mm. An average of results from two runs gave amorphous solid, 12.5 g.; dibenzyl, 6.3 g.; tarry, carbonaceous residue, 14.5 g.

Table I provides essential data. Yields in each case are averages from two runs.

Summary

1. The reaction of α,β-dichloropropionaldehyde with phenylmagnesium bromide, n-hexylmagnesium bromide, cyclohexylmagnesium bromide, β-phenylethylmagnesium bromide and benzylmagnesium chloride has been studied.

2. The new secondary alcohols 2,3-dichloro-1-phenylpropanol-1, 1,2-dichlorononanol-3, 2,3-dichloro-1-cyclohexylpropanol-1 and 1,2-dichloro-5-phenylpentanol-3 have been prepared via the Grignard reaction.

AKRON, OHIO RECEIVED MARCH 17, 1948

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1162]

Cyclobutane Derivatives. IV. Ziegler Bromination[1a] of Methylenecyclobutane[1b,2]

BY EDWIN R. BUCHMAN AND DAVID R. HOWTON

In connection with another investigation,[3] we have studied the reaction,[1a] under a variety of conditions, between N-bromosuccinimide (NBS) and methylenecyclobutane (I). It was found that, although NBS reacted with I faster in the usually employed carbon tetrachloride[1a] than in benzene,[4] higher yields of allylic bromides, C_5H_7Br, were obtained in the latter solvent; in both cases the addition of small amounts of dibenzoyl peroxide[5] proved advantageous. A typical experiment carried out in benzene and with added peroxide gave the following products[6]: a C_5H_7Br fraction (14%), methylenecyclobutane dibromide[7] (56%), N-phenylsuccinimide[9] (15%) and succinimide (66%). In carbon tetrachloride and without added peroxide another minor product was encountered, apparently formed by direct 1:1 addition[8] of NBS to I.

The C_5H_7Br mixture (II + III) was investigated as indicated on the diagram. II and III were separated by virtue of the great difference in the rates at which they react with trimethylamine in benzene at room temperature. III reacted in a few minutes to precipitate the corresponding[10] allylic quaternary ammonium bromide (V) while the complete conversion of II to IV required several weeks; the relative amounts of IV and V isolated indicate a II:III ratio in the C_5H_7Br fraction of about 15:1.

The structure[11] of V (and indirectly that of IV) was established by relating it to the known[13] saturated quaternary bromide (IX). In this connection the applicability of a recently described[12] two-step reduction method was investigated. The addition of bromine to V yielded a single dibromo bromide to which structure VII must be assigned since on catalytic hydrogenation it was converted to a bromide identified (by comparison with an authentic sample[13]) as IX. However, the bromination of IV gave not only compound VI isomeric with VII (and yielding on reduction VIII isomeric with IX) but also, by a novel rearrangement, a nearly equal amount of bromide VII identical with the material originating from V.

A structure proof based on reactions not accompanied by possible rearrangements was achieved

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(1) (a) *Cf.* Ziegler, Späth, Schaaf, Schumann and Winkelmann' *Ann.*, **551**, 80 (1942); (b) *cf.* Ziegler bromination of ketene dimer' Blomquist and Baldwin, THIS JOURNAL, **70**, 29 (1948).

(2) Presented before the Pacific Division of the American Association for the Advancement of Science at the San Diego Meeting, June, 1947.

(3) See Paper V of this Series, to be published.

(4) *Cf.* Ettlinger and Fieser, *J. Biol. Chem.*, **164**, 451 (1946).

(5) *Cf.* Schmid and Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

(6) Yields based on NBS.

(7) Földi[8] obtained saturated dibromides from reactions of N-bromo-N-methylbenzenesulfonamide with certain olefins. In this Laboratory it has been found that I and cyclobutene,[3] which react slowly with NBS, give dibromides as major products (yield apparently independent of added peroxide but dependent on nature of solvent, see Experimental), while cyclohexene,[9] which reacts rapidly, gives only a small amount of dibromide.

The mechanism of formation of the dibromides remains obscure. Földi's unsubstantiated explanation that substituted derivatives of ethylenediamine and substituted dibromides are formed in equivalent amount obviously cannot apply in the present case. The possibility that hydrogen bromide (which would combine with NBS to make free bromine available, *cf.* Meystre, Ehmann, Neher and Miescher, *Helv. Chim. Acta*, **28**, 1252 (1945); Wieland and Miescher, *ibid.*, **30**, 1876 (1947); Barnes, THIS JOURNAL, **70**, 145 (1948)) is formed during the slow reaction is unsupported by experimental evidence; brominated reaction products from I appear to be stable and no loss of hydrogen bromide was noted during the Ziegler reaction or during the working-up procedure.

Cf. Buckles, Organic Division Abstracts, April, 1948, page 36L.

(8) *Cf.*. Földi, *Ber.*, **63**, 2257 (1930); Lichoscherstow, *et al.*, *Chem. Zentr.*, **109**, I, 3330 (1938); **110**, II, 66 (1939); **111**, I. 3246 (1940); **111**, II, 198 (1940); Kharasch and Priestly, THIS JOURNAL, **61**, 3425 (1939); Fosdick, Fancher and Urbach, *ibid.*, **68**, 840 (1946); ref. 1a.

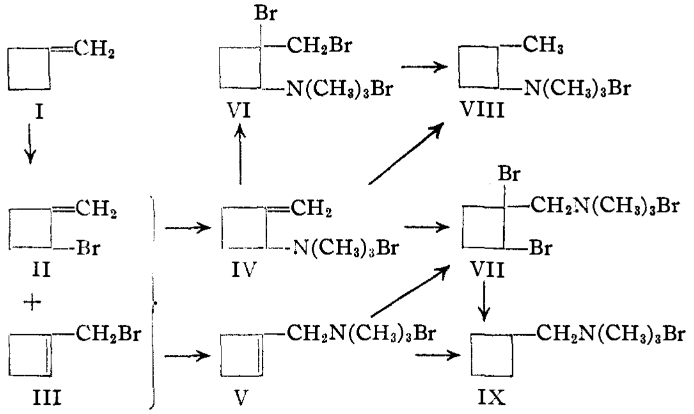
(9) *Cf.* Howton, THIS JOURNAL, **69**, 2060 (1947).

(10) The precipitated fractions are quite pure; we assume that III is the precursor of V and II of IV.

(11) As a possible aid in assigning structures to such compounds, it may be noted that there appears to be a degree of correspondence in m. p.'s between allylic quaternary picrates and the related saturated picrates, *e. g.*, picrates corresponding to V and IX melt at 127 and 117°, respectively, while for the IV–VIII pair the values are 215 and 245°; Howton[12] gives: 2-cyclohexenyltrimethylammonium picrate, m. p. 130°, and cyclohexyltrimethylammonium picrate, m. p. 125°; allyltrimethylammonium picrate, m. p. 220°, and n-propyltrimethylammonium picrate, m. p. 200°.

(12) Howton, THIS JOURNAL, **69**, 2555 (1947).

(13) (a) v. Braun, Fussgänger and Kuhn, *Ann.*, **445**, 201 (1925); see also (b) Demjanow and Dojarenko, *Ber.*, **55**, 2727 (1922); *Chem. Zentr.*, **94**, III, 746 (1923).



by the direct catalytic reduction of IV and of V. From V, IX was obtained, while IV gave a relatively good yield[14] of VIII identical with the reduction product from VI; this synthesis of VIII incidentally confirms the formulas assigned to both VI and VIII.

This research was aided by a grant from the Research Corporation; the authors wish also to express their thanks to Dr. Saul Winstein and to Dr. Martin G. Ettlinger for helpful discussions.

Experimental[15]

Ziegler Bromination of I.—A two-liter three-necked flask was charged with 178 g. (1.0 mole) of NBS,[1a] 2.42 g. (0.01 mole) of dibenzoyl peroxide, 71.0 g. (1.044 mole) of I[16] and 740 ml. of thiophene-free benzene (dried over sodium); the flask was equipped with a mercury-sealed Hershberg stirrer, a water-cooled reflux condenser topped by another containing Dry Ice, and a thermometer dipping into the reaction mixture. The stirred mixture was maintained at 75–80° (gentle reflux) by means of a heating mantle. From time to time the reaction mixture was cooled to about 40° and a drop of liquid was removed and tested with aqueous potassium iodide for the presence of NBS; after six and one-half hours the test was negative. After standing overnight at room temperature, 57.9 g. of crystalline solid (A) was filtered from the brown mixture; 11.6 g. of I was recovered from the filtrate by distillation at atmospheric pressure, using a 30-cm. helix-packed column. Most of the benzene was then removed through the same column at 200 mm. On standing overnight, 19.7 g. of solid (B) crystallized from the residue. The filtrate from B was then distilled rather rapidly through a 9-cm. helix-packed column with efficient condensation (Dry-Ice trap) of the distillate, first at 70 mm. and then at 30 mm. until all of the allylic bromides had been removed. The resulting distillate was refractionated through the same column giving 21.6 g. (14.6%[6]) of a mixture of II and III, b. p. 55.2–56.7° at 70 mm. This material rapidly decolorized potassium permanganate in acetone solution, slowly decolorized bromine in carbon tetrachloride, gave an immediate precipitate with alcoholic silver nitrate and slowly darkened on standing at room temperature exposed to light.

Anal.[17] Calcd. for C_5H_7Br: C, 40.84; H, 4.80; Br, 54.36. Found: C, 40.83; H, 5.11; Br, 54.78.

The residual oil from the rapid initial distillation of the C_5H_7Br fraction deposited 12.1 g. of crystalline material (C) on standing; this was filtered off and the filtrate combined with a small amount of oil left from the final fractionation of the C_5H_7Br distillate and distilled at 3 mm., giving 65.1 g. (56.2%[6]) of I dibromide, pale yellow subtly lachrymatory oil, b. p. 43–50°, n^{25}_D 1.532,[17] d^{25}_4 1.801[17]; this material[18] decolorized permanganate in acetone rapidly and formed a precipitate soon after mixing with a benzene solution of dimethylamine.

Removal of I dibromide from the reaction mixture left 43.8 g. of dark brown, very viscous oil which deposited 1.8 g. of crystalline material (D) after standing several months. Careful examination of the four crops of crystalline material showed A to be substantially pure succinimide, B and D to be N-phenylsuccinimide[9] and C to be a mixture of these two substances; total yield[6] of the first 66%, of the latter 15%. A fractional distillation *in vacuo* was carried out on the 42 g. of residual oil; small additional amounts of succinimide and of N-phenylsuccinimide were obtained but no other homogeneous product was isolated.

Reactions of this type gave consistently approximately the yields of bromination products indicated above; a bromination in benzene but without added peroxide required eleven and one-half hours and yielded[6] 9.1% of allylic bromides and 57.1% of the dibromide. In carbon tetrachloride the results were less consistent; figures[6] are given for two representative runs; 8.8% of allylic bromides and 52.8% of dibromide (two and one-half hours, 1.6 mole % peroxide), 5.6% of bromides and 34.1% of dibromide (three and one-half hours, no peroxide added). In *n*-heptane with 1.6 mole % peroxide the reaction appeared complete after two hours; 6.0% of monobromides and 24.3%[6] of dibromide were isolated from the gummy reaction mixture. Using excess of I as solvent and with added peroxide, no appreciable bromination took place even after twenty hours of refluxing.

From an experiment carried out in carbon tetrachloride (no added peroxide), it was found possible to isolate a small amount of a slightly colored, very viscous oil, b. p. 79° at 0.25 mm., which gave analytical figures close to those calculated for the adduct of I and NBS; it was difficult to completely free this oil from succinimide by distillation.

Anal. Calcd. for $C_9H_{12}BrNO_2$: C, 43.92; H, 4.92; N, 5.69. Found: C, 44.46; H, 5.31; N, 6.16.

(2-Methylenecyclobutyl)-trimethylammonium Bromide (IV) and (1-Cyclobutenylmethyl)-trimethylammonium Bromide (V).—The above mixture of II and III (21.6 g.) was treated in a centrifuge bottle with 63 g. (slight excess) of an 18% solution of trimethylamine in C. P. benzene. A voluminous crystalline precipitate (V) formed immediately; after standing for fifteen minutes at room temperature, this product was separated by centrifugation, washed with benzene and dried *in vacuo*, yield 1.4 g. (4.6%). Crude V, m. p. 162.5° (prior sintering), was found to be extremely hygroscopic (in other experiments V was obtained as an oil); it decolorized permanganate[19] rapidly and was characterized by conversion

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[14] Whereas V behaved normally[12] on reduction, giving trimethylamine as a major reaction product, IV yielded somewhat better than 50% of VIII. Seemingly IV does not possess a fully effective allylic double bond.

[15] All melting points are corrected. Microanalyses by Dr. G. Oppenheimer and G. A. Swinehart of this Institute.

[16] B. p. 40.0–42.3°; preparation, see Shand, Schomaker and Fischer, THIS JOURNAL, **66**, 636 (1944); a portion of the material used in this research was prepared by Mr. J. R. Fischer.

[17] These figures were obtained from a sample prepared in a similar fashion from a Ziegler bromination carried out in carbon tetrachloride.

[18] An authentic sample of I dibromide, b. p. 41–45° at 2.2 mm., n^{24}_D 1.537, decolorized permanganate and gave with dimethylamine the same series of reaction products (to be described in another connection).

[19] The behavior of quaternary bromides and picrates toward potassium permanganate in acetone or acetone–water solution was investigated. The unsaturated bromides IV and V as well as the corre-

to the quaternary picrate,[19,20] large dark yellow striated blades from ethanol–acetonitrile, m. p. 126.6–127.1° (analysis see below).

A small amount of material (0.4 g.) which deposited in the next seventy-five minutes was shown (by conversion to the picrate[20]) to be predominantly IV. After the benzene solution had stood tightly stoppered for two weeks longer, a dense network of colorless needles had formed which was centrifuged off (16.2 g. of IV); two months later another crop (4.6 g.) was collected; total yield of crystalline IV, 70%. A small amount of oily material (crude IV) subsequently separated from the benzene solution and there remained a certain amount of bromine-containing benzene-soluble material which apparently did not react with trimethylamine.

Fractional crystallization of the IV obtained above and examination of the mother liquors (by conversion to the picrate[20]) failed to disclose the presence of any appreciable amount of V. IV[19] formed hygroscopic sparse clusters of colorless rods from acetone–ethanol, m. p. 229° dec.

Anal. Calcd. for $C_8H_{16}BrN$: C, 46.61; H, 7.82; N, 6.80. Found: C, 47.17; H, 8.07; N, 6.60.

The picrate[19,20] corresponding to IV crystallized from ethanol in long yellow feathers, m. p. 215–217° dec.

Anal. Calcd. for $C_{14}H_{18}N_4O_7$: C, 47.46; H, 5.12; N, 15.81. Found (IV picrate): C, 47.51; H, 5.41; N, 15.85. Found (V picrate): C, 47.47; H, 5.36; N, 15.59.

Bromination of IV.—A solution of 1.41 g. of IV (as obtained from the benzene–trimethylamine solution) in 5 ml. of chloroform was treated with 1.10 g. (one molecular equivalent) of bromine; the resulting two-liquid-phase mixture was tightly stoppered and allowed to stand at room temperature for ten days. The crop of clustered jagged crystals (VI) which had emerged from the pale orange solution was freed of mother liquors by rinsing with chloroform and dried, m. p. 203.5° dec., yield 1.02 g. (41%). A sample was recrystallized from ethanol–water, colorless truncated dog-tooth-like crystals, some arranged in rows to form long, irregular blades, m. p. 195.5° dec.[21] (analysis below).

The mother liquors and washings from this crop of VI were freed of solvent and rapidly diluted with acetone, giving a voluminous white crystalline precipitate of crude VII weighing 0.93 g. (37%), m. p. *ca.* 168°. This was recrystallized by dissolving in a small amount of warm methanol and rapidly diluting with acetone, broad colorless plates with bluntly pointed terminations, m. p. 163–164° dec.[21]

Anal. Calcd. for $C_8H_{16}Br_3N$: C, 26.25; H, 4.41; N, 3.83. Found (VI): C, 26.19; H, 4.85; N, 3.74. Found (VII): C, 26.77; H, 4.64; N, 3.77.

Another bromination of IV (procedure similar to that used for bromination of V, see below) gave a 33% yield of VI and a 27% yield of VII (isolated as the picrate). VII obtained in this manner and the corresponding picrate were compared (mixed m. p.'s gave no depression) with material from bromination of V. VII from bromination of IV was also converted (see below) to IX and its picrate (mixed m. p.'s).

The quaternary picrate corresponding to VI was recrystallized from ethanol–water, yellow rhombic plates, some with striations parallel to all four edges of the rhombs, others growing to a point in such a way as to form stubby triangular prisms, m. p. 173°.[21] The picrate corresponding to VII, orange-yellow bars or granules from ethanol–water, melted at 172°.[21] A mixture of the two isomeric picrates gave a difficultly-detectable depression of the melting point.

Anal. Calcd. for $C_{14}H_{18}Br_2N_4O_7$: C, 32.70; H, 3.53. Found (VI picrate): C, 32.80; H, 3.55. Found (VII picrate): C, 32.99; H, 3.60.

Bromination of V.—A solution of 1.09 g. of crude crystalline V in 4 ml. of chloroform was treated dropwise with bromine until a heavy oil separated out; the mixture was then diluted with benzene and treated with more bromine until the color of the latter persisted in the benzene epiphase. The heavy oil was then thoroughly washed with benzene, taken up in 25 ml. of ethanol and slowly freed of solvent on the steam-bath; the residual clear tan sirup was taken up in 10 ml. of acetone and placed in an ice-box overnight, giving rise to 0.65 g. of VII, compact rosettes, crude m. p. 170° dec. Mother liquors yielded an additional 0.24 g. of VII, crude m. p. 169° dec. and 0.57 g. of crude VII picrate[22] (total yield of VII, 66.5%).

(2-Methylcyclobutyl)-trimethylammonium Bromide (VIII).—Recrystallized IV (0.90 g.) was added to a suspension of pre-reduced palladium-on-barium-sulfate catalyst[12] (2.25 g.) in 25 ml. of water and the mixture was shaken with hydrogen at room temperature and atmospheric pressure. After nineteen hours the absorption rate was negligible and 155.8 ml. of hydrogen had been absorbed (theory for one mole-equivalent, 112 ml.). The catalyst was centrifuged off, the solution was treated with sodium hydroxide in slight excess and the liberated trimethylamine was removed on the steam-bath *in vacuo*. Then, after neutralization with hydrobromic acid, the solution was evaporated to dryness. The residue was extracted with chloroform and the extracts were freed of solvent and treated with acetone; in this way three crops of crude VIII were obtained totaling 0.41 g. (45%) and from the mother liquors 0.11 g. of VIII picrate (total yield of VIII, 52%). VIII picrate made from this crude VIII did not depress the m. p. of a like picrate obtained from VI (see below).

Catalytic reduction[12] of VI gave a theoretical yield of crude VIII; after recrystallization from acetone–methanol, it formed colorless plates of various rectangular shapes, m. p. 270° dec.

Anal. Calcd. for $C_8H_{18}BrN$: C, 46.16; H, 8.71; N, 6.73. Found: C, 46.04; H, 8.97; N, 6.10.

The corresponding picrate formed bundles of yellow needles from ethanol, m. p. 244.6–244.8°.

Anal. Calcd. for $C_{14}H_{20}N_4O_7$: C, 47.19; H, 5.66. Found: C, 47.24; H, 5.81.

(Cyclobutylmethyl)-trimethylammonium Bromide (IX).—Reduction[23] of cyclobutyl cyanide[24] in ethanol–12 *N* hydrochloric acid using a palladium-on-Norit catalyst gave cyclobutylmethylamine hydrochloride, characteristic colorless flakes from acetone–ethanol, m. p. 235.5°. This hydrochloride (1.54 g.) was methylated in the usual way[13b] with methyl iodide and potassium hydroxide in methanol. After removal of solvent the product was separated by continuous extraction with chloroform, yield of crude (cyclobutylmethyl)-trimethylammonium iodide nearly quantitative (3.18 g.); recrystallization from acetone–ethanol gave glistening colorless needles, m. p. 205.6–206.5°.

Anal. Calcd. for $C_8H_{18}IN$: C, 37.66; H, 7.11; N, 5.49. Found: C, 37.80; H, 6.96; N, 5.48.

The iodide was converted to the base with silver oxide and this after neutralization with hydrobromic acid gave

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sponding picrates decolorized permanganate rapidly while VI, VII, VIII and IX and their picrates did not. The stability of VI is of interest since I dibromide reacts readily with permanganate under these conditions, see ref. 18.

(20) See ref. 12, footnote 5.

(21) Melting point bath heated slowly; m. p. varies considerably with rate of heating.

(22) Mother liquors from this picrate gave 0.45 g. of material m. p. below 95°, from which, after several recrystallizations, a homogeneous substance was obtained, sparsely-clustered thin rectangular slats from ethanol–acetonitrile, m. p. 142.5–143.2°, halogen-free, unsaturated to permanganate. This may be (2-methyl-2-butenyl)-trimethylammonium picrate derived from 2-methylbutene-1 originally present (see footnote 8 of ref. 16) as an impurity in I.

Anal. Calcd. for $C_{14}H_{20}N_4O_7$: C, 47.19; H, 5.66; N, 15.72. Found: C, 47.25; H, 5.73; N, 15.75.

(23) *Cf.* Hartung, THIS JOURNAL, **50**, 3370 (1928).

(24) B. p. 147–148° (747 mm.), prepared in 62% yield according to Freund and Gudeman, *Ber.*, **21**, 2697 (1888).

IX, beautiful sparse clusters of colorless triangular prisms from acetone–methanol, m. p. 220–221° (lit.[13a] m. p. 214°). Another sample of IX (from reduction of VII) exhibited dimorphism; on seeding a supercooled solution of the material in acetone–methanol, colorless needles were rapidly deposited which changed into massive granules, the interconversion being complete in about three hours at 0°. These granules melted at 219.6–220.2°, resolidified on withdrawing from the bath, then melted at 226°; a sample mixed with authentic IX showed the same behavior.

Anal. Calcd. for $C_8H_{18}BrN$: C, 46.16; H, 8.71; N, 6.73. Found: C, 45.75; H, 8.77; N, 6.39.

The above salts gave the corresponding picrate, bright yellow-orange dendrites from ethanol, m. p. 116.5–117.1°.

Anal. Calcd. for $C_{14}H_{20}N_4O_7$: C, 47.19; H, 5.66; N, 15.72. Found: C, 47.40; H, 5.75; N, 15.50.

The halides with excess of aqueous sodium picrate gave a picrate–sodium picrate double salt,[20] fine yellow needles from ethanol, m. p. 164.4–164.7° (prior sintering).

Anal. Calcd. for $C_{14}H_{20}N_4O_7 \cdot C_6H_2N_3NaO_7 \cdot 0.5H_2O$: C, 38.97; H, 3.76; N, 15.91; Na, 3.73. Found: C, 38.83; H, 4.04; N, 16.26; Na, 3.39.

Catalytic reduction[12] of VII gave in good yield IX (mixed m. p. with authentic IX) which was converted to the picrate (mixed m. p.). A very small yield of IX (isolated as the picrate–sodium picrate double salt, mixed m. p. and analysis) resulted from the reduction[12] of crude V using a palladium-on-Norit catalyst; trimethylamine hydrobromide constituted the major reaction product.

Summary

The Ziegler bromination of methylenecyclobutane has been studied. The major bromination product is the olefin dibromide and under the best conditions found (in benzene and with added peroxide) the yield of allylic bromides is 14%.

The allylic bromides were investigated by conversion to the allylic trimethylammonium bromides, the structures of which were established.

PASADENA 4, CALIFORNIA RECEIVED MARCH 15, 1948

[CONTRIBUTION FROM THE COATES LABORATORIES OF LOUISIANA STATE UNIVERSITY]

Analysis of the Vibrations of Benzene Derivatives. I. The Class A_1 Carbon Vibrations of Toluene

BY A. R. CHOPPIN AND C. H. SMITH[1,2]

The assignment of experimentally observed vibrational frequencies of aromatic molecules to definite modes of vibration has encountered difficulties, chief of which has been the large number of vibrations belonging to each symmetry class. Only for the highly symmetrical benzene molecule has it been possible to make assignments with confidence.

For toluene, the assignments have been more speculative. The polarization measurements in the Raman spectrum made by Cabannes and Rousset[3] and by Cleveland[4] have been of importance in identifying the totally symmetric vibrational frequencies. However, the number of observed polarized lines is less than the theoretical number of totally symmetric vibrations, even if toluene is assigned C_{2v} symmetry. Teets and Andrews[5] constructed a mechanical model of toluene, and found certain correlations between its vibrational frequencies and those observed in the Raman spectrum of toluene. Pitzer and Scott,[6] reasoning by analogy with benzene, assigned a frequency and vibrational form to each of the fundamental vibrations of the toluene molecule. However, except for the 1003 cm.$^{-1}$ frequency, they did not analyze the changes that occur in the vibrational forms on going from benzene to toluene. Ginsburg, Robertson and Matsen[7] have analyzed the near-ultraviolet absorption spectrum of toluene vapor and made a considerable number of frequency assignments.

Recently, the authors[8] have developed an interpretation of the ultraviolet absorption spectrum of toluene which differs from that of Ginsburg, Robertson and Matsen in that the 623 cm.$^{-1}$ frequency (in the ground state) is assigned to Class A_1 instead of Class B_1. Furthermore, the authors have proposed certain approximate vibrational forms for the Class A_1 carbon vibrations of toluene. These forms were based upon analogies with benzene and upon frequency changes taking place upon the substitution of deuterium for the various hydrogens of toluene. They differ in some cases from the forms assigned by Pitzer and Scott,[6] and from the forms observed in the mechanical model.[5]

In an attempt to settle these differences in the assignment of the frequencies and modes of vibration of toluene, the mathematical analysis presented in this article was made.

Calculations

In order to simplify the mathematical analysis, the carbon and hydrogen vibrations are treated as distinct uncoupled sets. This follows a previous qualitative treatment of the benzene vibrations.[9] For the purpose of the calculation of the carbon vibrations, it is assumed that each hydrogen is

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[1] American Chemical Society Post-doctoral Research Fellow at Louisiana State University.

[2] The authors are indebted to Newton Grant for checking some of the calculations.

[3] Cabannes and Rousset, *Ann. phys.*, **19**, 229 (1933).

[4] Cleveland, *J. Chem. Phys.*, **13**, 101 (1945).

[5] Teets and Andrews, *J. Chem. Phys.*, **3**, 175 (1935).

[6] Pitzer and Scott, THIS JOURNAL, **65**, 803 (1943).

[7] Ginsburg, Robertson and Matsen, *J. Chem. Phys.*, **14**, 511 (1946).

[8] Choppin and Smith, THIS JOURNAL, **70**, 577 (1948).

[9] Angus, Bailey, Hale, Ingold, Leckie, Raisin, Thompson and Wilson, *J. Chem. Soc.*, 971 (1936).