1-Butyl-3-pyrrolidone.—Dieckmann ring closure using sodium ethoxide in xylene at 120°[1] followed by hydrolysis and decarboxylation gave the aminoketone in 73% yield; b.p. 38° (0.5 mm.); n^{20}_{D} 1.4510; d^{20}_{4} 0.918.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.04; H, 10.71; *MR*D, 41.06. Found: C, 67.81; H, 10.70; *MR*D, 41.38.

The picrate of 1-butyl-3-pyrrolidone was obtained as fine yellow needles, m.p. 157.5–158°, with decomposition, after formation in ethanol and recrystallization from methanol.

Anal. Calcd. for $C_{14}H_{18}N_4O_8$: C, 45.41; H, 4.90. Found: C, 45.33; H, 5.17.

Ethyl β-N-(2-Carbethoxypyrrolidyl)-butyrate.—A solution of 25 g. (0.175 mole) of ethylproline and 100 g. (0.877 mole) of ethyl crotonate was heated at 100° for 48 hours.[9] The excess ethyl crotonate was removed by distillation at atmospheric pressure and the diester was obtained as a colorless liquid, b.p. 99–100° (0.3 mm.); n^{20}_{D} 1.4566; d^{20}_{4} 1.064; yield 13.8 g. (31%).

Anal. Calcd. for $C_{13}H_{23}NO_4$: C, 60.69; H, 8.98; N, 5.44. Found: C, 60.52; H, 8.96; N, 5.62.

1-Keto-3-methylpyrrolizidine.—The procedure of McElvain and Rorig[11] employing sodium hydride was used for the Dieckmann ring closure of ethyl β-N-(2-carbethoxypyrrolidyl)-butyrate. The aminoketone obtained in 50% yield after hydrolysis and decarboxylation was converted directly and no attempt was made to isolate both of the possible racemates. The hydrochloride was hygroscopic. **The picrate**, prepared in ether and recrystallized from methanol, separated as long yellow needles, m.p. 189–190°, with decomposition.

Anal. Calcd. for $C_{14}H_{16}N_4O_8$: C, 45.65; H, 4.37; N, 15.21. Found: C, 45.79; H, 4.43; N, 15.24.

The picrolonate, prepared in ether and recrystallized from ethanol, formed orange leaflets, m.p. 206–207°, with decomposition.

Anal. Calcd. for $C_{18}H_{21}N_5O_6$: C, 53.59; H, 5.25; N, 17.36. Found: C, 53.86; H, 5.32; N, 17.07.

Wolff–Kishner Reduction of 1-Keto-3-methylpyrrolizidine. 3-Methylpyrrolizidine.—A solution of 0.20 g. of 1-keto-3-methylpyrrolizidine, 1.0 g. of hydrazine hydrate (85%), and 1.0 g. of potassium hydroxide in 10 ml. of triethylene glycol was boiled under reflux for one hour. The solution was then distilled until the distillate was no longer basic. The distillate was saturated with potassium carbonate and extracted with ether. The ethereal solution was dried and treated with picric acid in ether. **The picrate** thus obtained crystallized from methanol as yellow elongated plates, m.p. 251–252°, with decomposition.

Anal. Calcd. for $C_{14}H_{18}N_4O_7$: C, 47.46; H, 5.12; N, 15.81. Found: C, 47.62; H, 5.12; N, 15.83.

The Clemmensen reduction of 1-keto-3-methylpyrrolizidine gave results which were inconclusive, however; the crude product yielded a small amount of $C_8H_{15}N$ picrate, m.p. 251–252° (dec.), which was found to be identical with the 3-methylpyrrolizidine picrate described above by mixed melting point and infrared absorption spectra determinations.

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(11) S. M. McElvain and K. Rorig, THIS JOURNAL, **70**, 1820 (1948).

THE NOYES CHEMICAL LABORATORY
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RECEIVED DECEMBER 8, 1950

The Optical Rotation of 2-Chlorobutane

BY ROBERT L. LETSINGER, LUCIEN G. MAURY AND ROBERT L. BURWELL, JR.

We have determined limiting values for the rotation of optically pure 2-chlorobutane by means of a displacement reaction with benzylsodium. The use of this reagent was suggested by the characteristics of its reaction with (+)2-bromobutane.[1]

Benzylsodium and 2-chlorobutane (α^{25}_{D} −10.93°) combined to give 1-phenyl-2-methylbutane with α^{25}_{D} + 3.26°. On the basis of α^{25}_{D} +9.9° ($[\alpha]^{25}_{\mathrm{D}}$ +11.6°) as the maximum rotation for this hydrocarbon,[1] therefore, α^{25}_{D} 33.2° is an upper limit for the rotation of optically pure 2-chlorobutane. The actual value may be somewhat lower since 9.9° is probably a little high for the hydrocarbon and some loss of asymmetry may have occurred in the benzylsodium condensation.

Of reported cases, the preparation of 2-chlorobutane which involved the least racemization was the conversion of 2-butanol ($[\alpha]^{25}_{\mathrm{D}}$ −5.54°) to 2-chlorobutane ($[\alpha]^{25}_{\mathrm{D}}$ + 13.70°).[2] Calculation of these data to the basis of optically pure alcohol ($[\alpha]^{25}_{\mathrm{D}}$ 13.64°)[3] gives α^{25}_{D} 29.2° (or $[\alpha]^{25}_{\mathrm{D}}$ 33.8°) as a rotation of 2-chlorobutane experimentally obtainable. The rotation for the pure enantiomorph must therefore lie between α^{25}_{D} 29.2° and 33.2°.

Experimental

The symbol, α^{25}_{D}, designates the homogeneous rotation in a 1 dm. tube.

2-Chlorobutane.—2-Butanol (5.66 g., α^{25}_{D} +7.48°, n^{25}_{D} 1.3944) was saturated with hydrogen chloride gas at zero degrees. The solution was then sealed in a tube and heated at 75° for 72 hours, during which time it separated into two layers. After cooling, the tube was opened and the contents washed successively two times with water, three times with concentrated hydrochloric acid, three times with concentrated sulfuric acid, and finally three times again with water. The 2-chlorobutane thus obtained was dried over calcium chloride; 6.8 g. product (96%); α^{25}_{D} −12.24°, n^{25}_{D} 1.3942. Two samples prepared in this manner were combined to give a product with α^{25}_{D} 10.93°; n^{25}_{D} 1.3942.

1-Phenyl-2-methylbutane.—Butylsodium was prepared as previously described[1] from *n*-butyl chloride (23.1 g., 0.25 mole) and sodium (11.5 g., 0.5 g. atom) with hexane as a solvent. To ensure complete reaction of the halide, the butylsodium was stirred two hours at 25° and then permitted to stand at room temperature for 20 hours. At the end of this time, toluene (160 cc.) was added and the mixture stirred for an additional six hours at 25°. Metalation was comparatively rapid as evidenced by the change from blue to green in less than ten minutes, and then to yellow in about half an hour.

A solution of 2-chlorobutane (8.67 g., 0.0937 mole, α^{25}_{D} −10.93°) in 10 cc. of hexane was added over a period of five minutes to the rapidly stirred suspension of benzylsodium, which was maintained at 15°. After an additional ninety minutes of stirring, the mixture was carbonated on powdered Dry Ice. The hydrocarbon portion was separated by conventional procedures and the 1-phenyl-2-methylbutane isolated by distillation; 7.63 g. (55%); b.p. 90–91° (27 mm.); α^{25}_{D} +3.26°, d^{25}_{4} 0.8544, n^{25}_{D} 1.4848.

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(1) R. L. Letsinger, THIS JOURNAL, **70**, 406 (1948).

(2) J. F. Lane and S. E. Ulrich, *ibid.*, **72**, 5132 (1950).

(3) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911). This value was interpolated from rotations measured at 20° and 50°.

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RECEIVED OCTOBER 21, 1950

An Analysis of the Electron Diffraction Data for Decaborane

BY CHARLYS M. LUCHT

Silbiger and Bauer[1] have presented their electron diffraction data for the molecular structure of decaborane, $B_{10}H_{14}$. They had tried all the molecular models which had been proposed in the literature up to that time and also calculated many others which might have been possible. The arrangement of planar hexagons suggested by Pitzer[2] and several

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(1) G. Silbiger and S. H. Bauer, THIS JOURNAL, **70**, 115 (1948).

(2) K. S. Pitzer, *ibid.*, **67**, 1136 (1945).

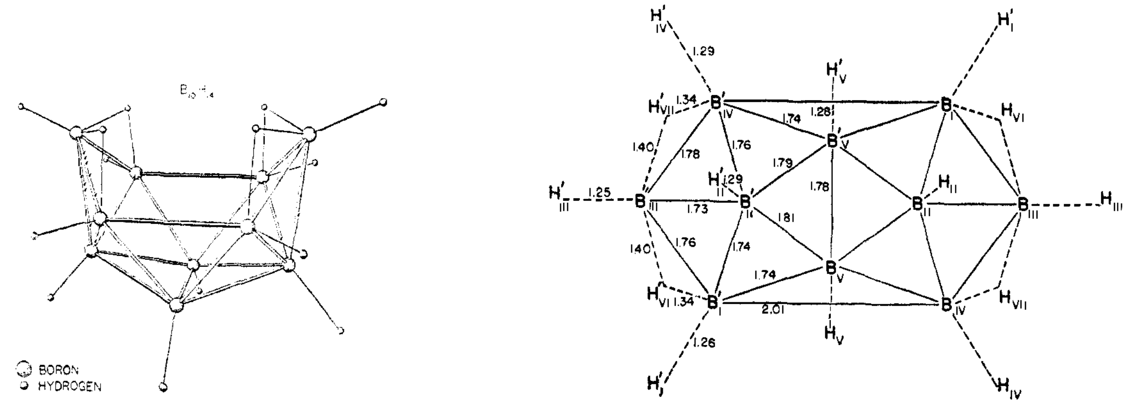
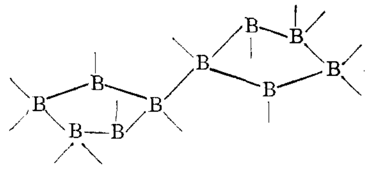


Fig. 1.—(a) Drawing of decaborane molecule. (b) Topological diagram of $B_{10}H_{14}$. The bond distances shown were determined from X-ray data.

other structures were eliminated by the work of Silbiger and Bauer. These authors found, moreover, that no previously proposed structure completely satisfied their data. Since that time the X-ray diffraction determination of the crystal structure has been completed[3] and has definitely established a molecular configuration which was not among those considered by Silbiger and Bauer. The molecular configuration found in the solid is in agreement with the available electron diffraction data. This was suggested in a preliminary way by Bauer in the terminal footnote of their paper (p. 119).

Figure 1 shows a drawing of the decaborane molecule which has the symmetry mm2. The boron atoms are at ten of the vertices of a somewhat distorted regular icosahedron, two neighboring vertices of which are unoccupied. The resulting arrangement forms two regular pentagonal pyramids with a common edge, and an angle of 76° between the base planes of the pyramids. All 14 of the hydrogen atoms were resolved in the Fourier maps calculated from the X-ray data. Each of 10 hydrogen atoms is attached to a single boron atom in the direction of a fivefold axis of the icosahedron. The remaining four hydrogen atoms each bridge two boron atoms.

Professor Bauer has kindly sent us his experimental results and we undertook the calculation of the electron diffraction intensity curves based on the structure described above. I.B.M. machines were used for these calculations, and the Watson Laboratories of I.B.M. furnished us a set of punched cards containing values of sin x/x. The intensity calculations were broken down to show the contributions of the boron framework, the B–H bonds, and the long, non-bonded B to H distances. The addition of the B–H terms changes the relative heights and positions of the maxima but does not affect the over-all qualitative agreement of the calculated curves with the observed intensities. One set of curves was calculated using the exact interatomic distances as determined by the X-ray data.[3] These distances are shown in the topological diagram of Fig. 1 and the complete intensity curve is reproduced in Fig. 2. This curve gave slightly better agreement with the electron diffraction data than a second set of curves which was calculated using averaged values of the bond lengths: B–B = 1.77 Å., B–H = 1.25 Å. and two B–B bonds of 2.00 Å. All of these curves show better agreement than any of the models proposed as "possible" by Silbiger and Bauer. Their "most probable" model, J, consisted of two regular pentagons in parallel planes with the interatomic distances B–B = 1.78 Å.,



B–H = 1.28 Å. and all angles tetrahedral except the pentagonal angles of 108°. The intensity curve for this model and the experimental curve are shown at the bottom of Fig. 2.

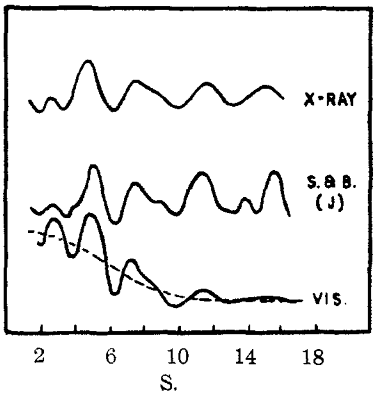


Fig. 2.—Intensity curves for decaborane. The top curve is typical of those calculated from models based on our X-ray results. The two lower curves are reproduced from Silbiger and Bauer's article.

The quantitative difference between the positions of the maxima and minima in the observed curve and the curve calculated from the X-ray coördinates is about 1.5%. No effort was made to improve this agreement since a better set of electron diffraction photographs using a rotating sector and heavier exposures would be necessary before any analysis of

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[3] J. S. Kasper, C. M. Lucht and D. Harker, *Acta Cryst.*, **3**, 436 (1950).

thermal motion of the boron and hydrogen atoms could be attempted.

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RECEIVED NOVEMBER 16, 1950

Preparation of Silver Colloid

BY GENTARO MATSUMURA

Finely pulverized magnesium oxide (5 g.) was kneaded with dilute aqueous silver nitrate solution (0.01 *N*, 5 cc.) crushed to a fine powder after drying at room temperature in desiccator, put into a graphite crucible and kept at 1010° for thirty minutes in a nichrome resistor furnace. Since it is well known that silver nitrate undergoes thermal decomposition at about 320° with the formation of silver nitrite and simultaneously the nitrite is further decomposed into metallic silver at that temperature,[1] on this heat-treatment finely dispersed crystals of silver nitrate are probably transformed into finely divided liquid silver droplets. After cooling, the reaction product was treated with excess of dilute acetic acid to dissolve magnesium oxide, filtered through filter paper and subjected to electrodialysis, giving a gray-pink colloidal solution of silver.

Spectral analysis showed that the particles of this colloidal solution consisted of metallic silver contaminated with a trace of magnesium.

I wish to express thanks to Prof. K. Iwase and Dr. K. Ogawa for continued advice and to Prof. R. Goto and Dr. N. Koizumi for performing the electrodialyses.

[1] M. Marcel Oswald, *Ann. chim.*, **6**, 32 (1914).

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RECEIVED JULY 16, 1950

Claisen Rearrangement of Allyl 3-(Trifluoromethyl)-phenyl Ether

BY E. T. MCBEE AND EDWARD RAPKIN[1]

An extensive survey of the literature[1a] reveals that little has been reported on Claisen rearrangement of negatively meta-substituted allyl phenyl ethers. The purpose of the investigation described in this paper was to determine the course of substitution when allyl 3-(trifluoromethyl)-phenyl ether and its homologs were made to undergo the Claisen rearrangement.

In agreement with previous observations,[2] the trifluoromethyl group appears to have a marked deactivating effect toward substitution in the phenol nucleus. Consequently, it was necessary to heat allyl 3-(trifluoromethyl)-phenyl ether for fifteen hours at reflux to achieve the same conversion in the Claisen rearrangement that can be obtained in one hour of heating allyl 3-methylphenyl ether.[3] Whereas it is usual for a methallyl ether to rearrange more rapidly than the corresponding allyl ether,[4] under similar reaction conditions methallyl 3-(trifluoromethyl)-phenyl ether did not give evidence of rearrangement during a twelve-hour reflux period.

Claisen rearrangement of allyl 3-(trifluoromethyl)-phenyl ether gives 2-allyl-5-(trifluoromethyl)-phenol. The structure of this material was demonstrated by conversion to 2-allyl-5-(trifluoromethyl)-anisole and subsequent oxidation to 2-methoxy-4-(trifluoromethyl)-benzoic acid. Synthesis of this acid was independently accomplished from 2-bromo-5-(trifluoromethyl)-anisole by halogen–metal interconversion with butyl lithium and carbonation of the resultant 2-methoxy-4-(trifluoromethyl)-phenyl lithium. Also oxidation of 2-propyl-5-(trifluoromethyl)-anisole, obtained by hydrogenation of the allylphenol followed by methylation of the product gave 2-methoxy-4-(trifluoromethyl)-benzoic acid.

Similar mechanisms for the Claisen rearrangement of allyl phenyl ether have been advanced in slightly different form by several investigators.[5,6,7] An essential step of the proposed mechanism involves the transfer of an electron pair from a carbon atom of the aromatic nucleus to the γ-carbon of the allyl group. On this basis it is reasonable to expect that allyl attack should occur at the carbon atom of highest electron density ortho to the allyloxy grouping. In the case of ethers of 3-(trifluoromethyl)-phenol, carbon atom 6 should have a much greater electron density than carbon atom 2 since the trifluoromethyl group is strongly electronegative. Therefore, the formation of 2-allyl-5-(trifluoromethyl)-phenol on heating allyl 3-(trifluoromethyl)-phenyl ether is in conformity with logical predictions which can be made on the basis of the postulated mechanism for the Claisen rearrangement.

Experimental[8]

Allyl 3-(Trifluoromethyl)-phenyl Ether.—A mixture of 35 g. (0.25 mole) of potassium carbonate, 30 g. (0.25 mole) of allyl bromide, 40.5 g. (0.25 mole) of 3-(trifluoromethyl)-phenol,[9] and 200 ml. of acetone was heated at reflux temperature for twelve hours. During this period a heavy precipitate of potassium bromide formed. At the conclusion of the reaction period, water was added until the inorganic salts dissolved. The upper organic layer was removed and the aqueous phase extracted with ether. The combined organic solutions were extracted with 10% sodium hydroxide solution and dried with Drierite. After removal of the ether at atmospheric pressure, the residual yellow oil was distilled at reduced pressure to yield 41 g. of colorless allyl 3-(trifluoromethyl)-phenyl ether (b.p. 62.4–62.8° at 4 mm.), n^{20}_{D} 1.4562. Acidification of the sodium hydroxide extract gave 3 g. of unreacted 3-(trifluoromethyl)-phenol. The conversion to allyl 3-(trifluoromethyl)-phenyl ether was 80% and the yield was 86%.

Anal. Calcd. for $C_{10}H_9F_3O$: C, 59.4; H, 4.46. Found: C, 59.4; H, 4.74.

Methallyl 3-(Trifluoromethyl)-phenyl Ether.—A mixture of 35 g. (0.25 mole) of potassium carbonate, 42 g. (0.25 mole) of potassium iodide, 23 g. (0.25 mole) of methallyl chloride, 41 g. (0.25 mole) of 3-(trifluoromethyl)-phenol

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[1] This paper contains material abstracted from the doctoral thesis of Edward Rapkin.

[1a] D. S. Tarbell, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 29–47.

[2] E. T. McBee and E. Rapkin, THIS JOURNAL, **73**, 1325 (1951).

[3] L. Claisen and O. Eisleb, *Ann.*, **401**, 57 (1913).

[4] Q. R. Bartz, R. F. Miller and R. Adams, THIS JOURNAL, **57**, 371 (1935).

[5] C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

[6] H. B. Watson, *Ann. Repts. Chem. Soc.*, **1939**, 206.

[7] A. C. Cope and E. M. Hardy, THIS JOURNAL, **62**, 441 (1940).

[8] Microanalyses by Dr. H. Galbraith,

[9] F. Swarts, *Bull. sci. acad. roy. Belg.*, **113**, 241 (1913).