Anal. Calcd. for $C_{11}H_{11}ClO_4SN_2$: C, 43.64; H, 3.66. Found: C, 44.00; H, 3.80.

Ethyl Cyclopentyl Carbonate.—Following the method of Bollinger, Hayes and Siegel[8] for ethyl cycloalkyl carbonates this compound was obtained in 30% yield, b.p. 90–91° (19 mm.), $n^{20}\mathrm{D}$ 1.4318, $n^{25}\mathrm{D}$ 1.4300, $d^{20}{}_4$ 1.0218, $d^{25}{}_4$ 1.0182.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.37; H, 9.19.

Saponification of ethyl cyclopentyl carbonate with solid sodium hydroxide followed by distillation gave ethanol, b.p. 78°, $n^{20}\mathrm{D}$ 1.3635 (lit.[10] b.p. 78.5°, $n^{20}\mathrm{D}$ 1.3610); α-naphthylurethan derivative m.p. 78° (lit.[11] m.p. 78°) and cyclopentanol, b.p. 138–139°, $n^{20}\mathrm{D}$ 1.4524 (lit.[11] b.p. 139°, $n^{20}\mathrm{D}$ 1.4530); α-naphthylurethan derivative, m.p. 118° (lit.[14] m.p. 118°). The solid residue remaining after distillation gave a positive test for carbonate.

Cyclopentanone Oxime.—Following the method of Bousquet[16] for oximes this compound was obtained in 91% yield, m.p. 56.5° (lit.[17] m.p. 56°), b.p. 96–98° (18 mm.).

Cyclopentylamine.—In the 300-ml. liner of a high pressure hydrogenator were placed 26 g. (0.26 mole) of cyclopentanone oxime, 50 ml. of absolute ethanol and a slurry consisting of 5 g. of Raney nickel in 10 ml. of ethanol. Hydrogenation was complete in 35 minutes during which time the temperature rose from 60 to 73°. The mixture was filtered and fractionated to obtain 12.5 g. (56%) of cyclopentylamine and 5.75 g. (29%) of dicyclopentylamine.[18,19]

Cyclopentylamine was allowed to stand over solid potassium hydroxide; redistillation provided a center cut, b.p. 107–108° (760 mm.), lit.[20] b.p. 108°), $n^{25}\mathrm{D}$ 1.4472, $d^{25}{}_4$ 0.8512. Cyclopentylamine was characterized by its thiocyanate salt, m.p. 94.5 (lit.[21] m.p. 93–94°). N-Cyclopentylbenzenesulfonamide, m.p. 68.5–69.5°, was prepared from cyclopentylamine and benzenesulfonyl chloride by the usual procedure.[22]

Anal. Calcd. for $C_{11}H_{15}O_2SN$: S, 14.23. Found: S, 14.01.

In like manner N-cyclopentyl-*p*-toluenesulfonamide, m.p. 84°, was obtained.

Anal. Calcd. for $C_{12}H_{17}O_2SN$: S, 13.40. Found: S, 13.22.

Cyclopentylamine was further characterized by its phthalimide and phthalamic acid derivatives. To phthalic anhydride was added an equimolar amount of cyclopentylamine. The mixture warmed spontaneously; it was then heated at 145° for 20 minutes. The melt, which solidified on cooling, was ground in a mortar, extracted with 5% sodium hydroxide and filtered. The residue, N-cyclopentylphthalimide (crude yield 65%, purified yield 53%), was recrystallized from 95% ethanol, m.p. 99–100°. This compound was identical with that obtained from the Gabriel synthesis, m.p. and mixed m.p. 99–100°.

Anal. Calcd. for $C_{13}H_{13}O_2N$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.28; H, 6.20; N, 6.74.

The alkaline extract from N-cyclopentylphthalimide was made acid to congo red. The precipitate, N-cyclopentylphthalamic acid, was washed, dried and recrystallized from 50% ethanol, m.p. 143–144°.

Anal. Calcd. for $C_{13}H_{15}O_3N$: C, 66.93; H, 6.48; N, 6.01. Found: C, 67.08; H, 6.37; N, 6.28.

N-Cyclopentylphthalamic acid and N-cyclopentylphthalimide were converted each to the other. The acid was converted to the imide by heating at 145° for 30 minutes. Recrystallization from 95% ethanol gave N-cyclopentylphthalimide, m.p. 99–100°. This material was identical with that obtained from the Gabriel condensation, m.p. and mixed m.p. 99–100°.

The imide was hydrolyzed for 9 hours with boiling, 47% hydrobromic acid. After the mixture was cooled and filtered, the precipitate was washed with water, dried and recrystallized from 50% ethanol. The product, N-cyclopentylphthalamic acid, was identical with that previously obtained, m.p. and mixed m.p. 143–144°.

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[16] F. W. Bousquet, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 313.

[17] Reference 11, p. 262.

[18] Reductive ammonation of cyclopentanone and the Gabriel synthesis gave less favorable yields of cyclopentylamine.

[19] H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937, p. 92, reported that the hydrogenation of cyclopentanone oxime in alcohol yields 80% cyclopentylamine and 10% dicyclopentylamine. This experiment was not found in the reference cited by Adkins nor could it be found elsewhere in periodical literature. A private communication from Adkins confirms the authors' search of the literature but expresses belief in the authenticity of the experiment.

[20] J. Wislicenus and W. Hentzschel, *Ann.*, **275**, 325 (1893).

[21] R. A. Mathes, F. D. Stewart, and F. Swedish, Jr., THIS JOURNAL, **70**, 3455 (1948).

[22] Reference 11, p. 91.

Magnetic and Spectroscopic Studies on Triphenylboron Sodium[1]

BY TING LI CHU[2]

RECEIVED NOVEMBER 14, 1952

It has long been known that sodium reacts with triphenylboron to form a yellow addition compound having the chemical composition $(C_6H_5)_3BNa$ (I). Triphenylboron is not a free group and bears no resemblance to the triphenylmethyl group. However, its reduction product, the compound I, has an odd number of electrons and has been described as a free radical from its chemical behavior toward oxygen, iodine, triphenylmethyl, etc.[3] We might expect the compound I to have magnetic properties characteristic of the unpaired electron and it is the purpose of this work to carry out such investigations.

Triphenylboron was prepared by the reaction of phenylmagnesium bromide with boron trifluoride.[3,4] The product was sensitive toward oxygen, hence it was necessary to effect the purification by repeated distillation and recrystallization from ether under vacuum. A product with a melting point of 136° (uncor.) was obtained. I was then prepared by treating triphenylboron either in dry ether or dry tetrahydrofuran with excess of 40% sodium amalgam under high vacuum. This compound is yellow, only slightly soluble in ether but very soluble in tetrahydrofuran. To determine the composition of the product, aliquot portions of the tetrahydrofuran solution were analyzed for sodium and boron. Sodium was determined by hydrolyzing the solution and titrating liberated alkali with acid, boron was determined by the procedure of Fowler and Kraus.[5] The mole ratio Na/B was found by this analysis to be 0.97 ± 0.02.

Measurements of the magnetic susceptibility were made utilizing a Gouy balance. Measurements were made immediately after the preparation of a sample as a precaution against decomposition. A 10% solution of I in tetrahydrofuran was placed in a Pyrex tube (40 cm. length and 12 mm. diameter) and sealed off while under high vacuum. The sample was weighed in the magnetic field to give a result related to the algebraic sum of the paramagnetic susceptibility and the diamagnetic susceptibility of I as well as the diamagnetic susceptibility of the solvent. Corrections for the

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[1] Assisted by the joint program of the ONR and AEC.

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[3] E. Krause and H. Polack, *Ber.*, **59**, 777 (1926).

[4] H. E. Bent and M. Dorfman, THIS JOURNAL, **57**, 1259 (1935).

[5] D. E. Fowler and C. A. Kraus, *ibid.*, **62**, 1143 (1940).

two diamagnetic contributions to the total susceptibility was made by making a second measurement on the same sample after chemically destroying the source of the paramagnetism. This measurement was effected by admitting air to the sample until decolorized and then repeating the weighing in the magnetic field. If we assume the diamagnetic contribution of I not to be changed appreciably by treatment with air, the net difference in the two weighings is proportional to the paramagnetic susceptibility of I. These measurements were carried out at several field strengths ranging from 6,000 to 10,000 oersteds and the results showed no paramagnetism.

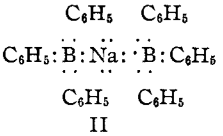
The paramagnetic resonance absorption results from the Larmor precession of the unpaired electron spin in an external magnetic field. The frequency of the radiation is

$$\nu = \frac{E_2 - E_1}{h} = \frac{g\beta H}{h}$$

where E_2 and E_1 are the energies of the two Zeeman levels of the unpaired electron spin, h is the Planck constant, g is the gyromagnetic ratio, β is the Bohr magneton and H is the magnetic field strength. The measurements were made on the apparatus constructed by Dr. J. Townsend of the Physics Department of Washington University,[6] it is sensitive for detecting 10^{-8} mole of free radicals. The frequency employed was about 9000 mc./sec., the measurement of resonance absorption was accomplished by modulating the magnetic field over a region which spans the resonant field for the applied radiofrequency. A tetrahydrofuran solution of I showed no absorption over a wide range of concentrations and magnetic field strengths; I also showed no absorption in the solid state. If the compound I had an unpaired electron spin, we would expect to observe the nuclear hyperfine structure arising from the interaction between the magnetic moments of the odd electron and the boron nucleus.

In a solvent of low dielectric constant, the compound I will exist as ion-pairs. The magnetic measurements indicate that the triphenylboron anion probably dimerizes to $(C_6H_5)_3B{:}B(C_6H_5)_3^{=}$ which is diamagnetic. There is evidence that trimethylgallium forms a colorless dimeric ion $Me_3Ga{:}GaMe_3^{=}$.[7] It is possible that there is an equilibrium between simple and dimeric triphenylboron anions which equilibrium, however, is shifted far toward the dimer under ordinary conditions.

Bent and Dorfman[4] observed the anomaly that when part of the sodium in I was removed by shaking with mercury or dilute amalgam, the yellow color entirely disappeared. The color change was reversible and they assumed that triphenylboron reacts with I to form a colorless addition product.



$$\begin{matrix} & \mathrm{C_6H_5} & & \mathrm{C_6H_5} & \\ \mathrm{C_6H_5{:}} & \underset{..}{\overset{..}{\mathrm{B}}} & \mathrm{{:}\underset{..}{\overset{..}{Na}}{:}{\cdot}} & \underset{..}{\overset{..}{\mathrm{B}}} & \mathrm{{:}C_6H_5} \\ & \mathrm{C_6H_5} & & \mathrm{C_6H_5} & \end{matrix}$$

II

This observation has also been confirmed in this Laboratory from the color change during the reaction between triphenylboron and sodium. However, the solutions obtained from various ratios of triphenylboron and sodium are all diamagnetic from paramagnetic resonance absorption and static susceptibility measurements. Furthermore, assuming that the triphenylboron anions are simple, we have no knowledge of how the presence of the sodium ion in the ion-pair would affect the properties of I in solution. The structure of formula II seems highly improbable. The color change might be accounted for by the equilibrium between simple and dimeric triphenylboron anions.

If I exists in a dimeric form in the solid state, the replacement of sodium by a bulky group, like tetraphenylstibonium group, appeared likely to bring about a dissociation into free radicals. However, the reaction product of I and tetraphenylstibonium hydroxide is diamagnetic in the solid state.

The absorption and fluorescence spectra of I were also measured in order to compare with those of triphenylmethyl. An ether solution of approximately 2×10^{-5} M sealed off under vacuum in a 1-cm. Pyrex cell was used for absorption measurement. The spectrum obtained at room temperature with a Beckman model DU spectrophotometer is given in Fig. 1,[8] it is quite different from that of triphenylmethyl. Triphenylmethyl shows seven weak absorption bands of extreme sharpness in the visible region which represent the vibrational terms in a single electronic band.[9] This set of absorption bands has an oscillator strength of the order of magnitude of 10^{-6} and these transitions probably arise from the slight distortion of planar configuration of the molecule and the perturbation by asymmetric vibrations.[10] The remarkable fine structures are also observed in other triarylmethyls. Triphenylmethyl also shows an intense absorption band in the near ultraviolet[11] representing an allowed electronic transition. I shows two intense absorption bands in the violet and near ultraviolet

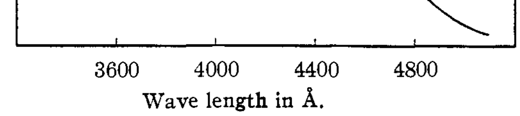


Fig. 1.—Absorption spectrum of triphenylboron sodium in tetrahydrofuran; approximate concentration 2×10^{-5} M.

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[6] Washington University, First Progress Report on Paramagnetic Resonance of Free Radicals under ONR contract N6onr-20205, December, 1951, p. 5.

[7] C. A. Kraus and F. E. Toonder, THIS JOURNAL, **55**, 3547 (1933).

[8] Because of the difficulty of measuring the exact concentration of I, optical density, instead of molar extinction coefficient, is plotted *versus* wave length.

[9] G. N. Lewis, D. Lipkin and T. T. Magel, THIS JOURNAL, **66**, 1579 (1944).

[10] S. I. Weissman and T. L. Chu, in preparation.

[11] L. C. Anderson, THIS JOURNAL, **57**, 1673 (1935).

with a separation of about 5,600 cm.$^{-1}$ between the peak maxima and the approximate oscillator strengths for these two transitions are 0.58 and 0.23, respectively. Even at low temperature, no fine structures could be observed within the experimental error. Most probably each absorption band represents a separate electronic transition.

A dilute solution of I in 4 parts ether and 1 part tetrahydrofuran[12] shows very strong fluorescence at 77°K. when illuminated with ultraviolet light. The fluorescence spectrum was photographed on a Steinheil spectrograph and the densitometer tracing of the spectral plate is reproduced in Fig. 2. The fluorescence of most organic molecules in condensed systems results from transitions from the fluorescent state down to the various vibrational levels of the ground state. Taking the normal state of I as zero, the position of the fluorescent level is 16,500 ± 50 cm.$^{-1}$ and the low lying vibrational levels are approximately located at 920 and 1,600 cm.$^{-1}$. The fluorescence of triphenylmethyl appears to be the mirror image of its absorption.[9]

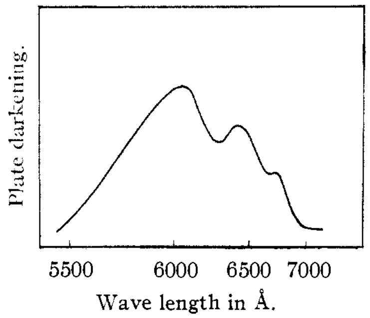

Fig. 2.—Fluorescence spectrum of triphenylboron sodium in 1:4 tetrahydrofuran–ether mixture.

Bent and Dorfman[13] prepared the disodium salt of tris-α-naphthylboron by treating tris-α-naphthylboron in ether solution with 40% sodium amalgam. It may be reported here that triphenylboron also forms dark green disodium salt by prolonged treatment with 40% sodium amalgam in tetrahydrofuran solution. The reversible color change similar to those reported for tris-α-naphthylboron disodium was also observed.

[12] This solvent mixture forms a rigid transparent medium at 77°K.

[13] H. E. Bent and M. Dorfman, THIS JOURNAL, **54**, 2132 (1932).

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Synthesis of Aureomycin Degradation Products. II

BY JAMES H. BOOTHE, R. G. WILKINSON, S. KUSHNER AND J. H. WILLIAMS

RECEIVED SEPTEMBER 29, 1952

Previous reports[1,2] have shown various phthalides and related compounds to be degradation products of aureomycin. These compounds have for the most part been synthesized for confirmation of structure. From a different portion of the aureomycin molecule some cyclopentane derivatives have been isolated,[3] two of which have been synthesized, namely, 1,3-cyclopentanedione and 1,2,4-cyclopentanetrione.

1,3-Cyclopentanedione was prepared from ethyl methyl β-ketoadipate[4] by cyclizing its ethylene ketal[5] with sodium ethoxide followed by hydrolysis and decarboxylation.

1,2,4-Cyclopentanetrione was prepared by treating diethyl oxalate and diethyl acetonedicarboxylate in the presence of sodium ethoxide to yield 3,5-dicarbethoxy-1,2,4-cyclopentanetrione. On hydrolysis and decarboxylation the triketone was obtained.

Richter[6] has described the preparation of 2-carbethoxy-1,3-cyclopentanedione. This compound was prepared in our laboratory and showed none of the properties expected. It could not be hydrolyzed and decarboxylated to the dione, it could not be oxidized to succinic acid, and it showed two C-methyl groups.

Ruggli and Maeder[7] have also reported the preparation of 2-carbethoxy-1,3-cyclopentanedione by the cyclization of methyl ethyl β-ketoadipate. They did not characterize the compound however and in our hands this reaction mixture after hydrolysis and decarboxylation did not yield 1,3-cyclopentanedione.

Ruggli and Doebel[8] prepared 2,4-dicarbethoxy-1,3-cyclopentanedione and have oxidized this with selenium dioxide to 3,5-dicarbethoxy-1,2,4-cyclopentanetrione. This compound, obtained in rather small amounts and not thoroughly purified or analyzed, melted approximately 20° below our best sample.

1,3-Cyclopentanedione and 1,2,4-cyclopentanetrione are quite acidic, the former having a pK_a of 4.5 and the latter a pK_a of 3.0. The ultraviolet absorption spectra of the dione show maxima at 257 mμ (E 29,400) in 0.1 N sodium hydroxide and at 242 mμ (E 20,700) in 0.1 N hydrochloric acid. The

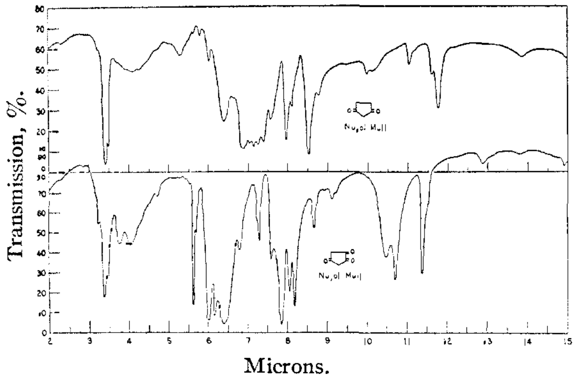

Fig. 1.—Infrared absorption spectra of 1,3-cyclopentanedione and 1,2,4-cyclopentanetrione.

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[1] B. L. Hutchings, C. W. Waller, S. Gordon, R. W. Broschard, C. E. Wolf, A. A. Goldman and J. H. Williams, THIS JOURNAL, **74**, 3710 (1952).

[2] S. Kushner, J. H. Boothe, J. Morton II, J. Petisi and J. H. Williams, *ibid.*, **74**, 3710 (1952).

[3] C. W. Waller, *et al.*, *ibid.*, **74**, 4978 (1952).

[4] J. C. Bardhan, *J. Chem. Soc.*, 1848 (1936).

[5] H. Schintz and G. Schappi, *Helv. Chim. Acta*, **30**, 1488 (1947).

[6] R. Richter, *ibid.*, **32**, 1123 (1949).

[7] P. Ruggli and A. Maeder, *ibid.*, **26**, 1476 (1943).

[8] P. Ruggli and K. Doebel, *ibid.*, **29**, 600 (1946).