

TABLE I
GERMANIUM TETRACHLORIDE
Three photographs; camera distance, 10.43 cm.;
 $\lambda = 0.0606 \text{ \AA.}$

Max.	Min.	$\frac{4\pi \sin \theta/2}{\lambda}$	x	$a = \text{Ge-Cl}$
1		4.088	8.17	(2.000)
	2	5.305	10.65	(2.008)
2		6.273	13.22	2.108
	3	8.598	17.82	2.074
3		9.750	20.29	2.080
	4	11.07	22.76	2.056
4		12.75	27.33	2.143
	5	14.24	29.82	2.094
5		15.46	32.20	2.082
	6	17.02	36.86	2.164
6		18.51	39.35	2.123
				Average 2.103

Ge-Cl = $2.10 \pm 0.03 \text{ \AA.}$
(Wierl, $2.10 \pm 0.05 \text{ \AA.}$)

TABLE II

Bond	Observed distance	Radius sum	Difference
C-Cl	1.76	1.76	0.00
Si-Cl	2.02	2.16	.14
Ge-Cl	2.10	2.21	.11
Sn-Cl	2.29	2.39	.10

distinction between these three and carbon tetrachloride can scarcely be explained on the basis of gradations in electronegativity of the central atoms. It seems probable that there is some essential difference in the character of the bond, such as the formation of double electron pair bonds as discussed in the previous report.

Studies of the tetramethyl compound are being made in the further investigation of this point.

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L. BROCKWAY

RECEIVED APRIL 1, 1935

OCCURRENCE OF ANABASINE IN NICOTIANA GLAUCA R. GRAH. (SOLANACEAE)

Sir:

Beta-pyridyl- α' -piperidine, $C_{10}H_{14}N_2$, isomeric with nicotine, was shown by Orechhoff and Menschikoff [*Ber.*, 64, 266 (1931)] to be present in the plant *Anabasis aphylla* L. (Chenopodiaceae) and was named "anabasine." Pictet and Rotschy had previously [*ibid.*, 34, 696 (1901)] reported β -pyridyl- α' -piperidine, which they called "nicotimine," to be present in tobacco in a ratio of 1 part of nicotimine to 200 parts of nicotine. Later work has shown that Pictet and Rotschy did not isolate the proper compound, but recently Ehren-

stein [*Arch. Pharm.*, 269, 627 (1931)] has apparently isolated the alkaloid anabasine from tobacco.

Schmuck [Krasnodar (U. S. S. R.) State Inst. Tobacco Invest., *Bull.* 109, 24 (1934)] stated that the alkaloid of *Nicotiana glauca* R. Grah. was not nicotine, but no identification was made. A sample of *Nicotiana glauca* roots was sent to this Laboratory by Mr. B. McKinney of the Tempe, Ariz., station of the Division of Truck Crop and Garden Insect Investigations of this Bureau. When examined it was found to contain about 1% of anabasine. A sample of the whole plant was later received from the same source and the identity confirmed by botanists of this Department. Further examination of samples of dried leaves from plants grown from seeds on the Arlington Experiment Farm by the Bureau of Plant Industry showed that they also contained anabasine. It is doubtful that nicotine is present except possibly in a trace.

The anabasine isolated was a liquid alkaloid boiling at 281° (537.8°F.) (corr.), which was soluble in water in all proportions and formed a picrate whose melting point of $212\text{--}213^\circ$ ($413.6\text{--}415.4^\circ\text{F.}$) was unchanged by admixture with picrate of anabasine prepared from commercial anabasine sulfate. The optical rotation $[\alpha]^{20}_D$ was -9.1° , instead of -82.2° reported by Orechhoff and Menschikoff, or -59.66° reported by Nelson [THIS JOURNAL, 56, 1989 (1934)]. Dehydrogenation by palladium black produced α, β -dipyridyl, which was formed into the dipicrate and the monopicrate, comparing closely with known samples of these picrates in appearance and melting points.

The principal method used to extract the anabasine was to digest the material with warm 1% hydrochloric acid, filter, make alkaline and extract with ether. When the alkaline solution was distilled, ammonia and pyridine were found in the first part of the distillate but nicotine was not detected. The removal of the anabasine by further distillation was incomplete.

Nicotiana glauca grows wild in various parts of the Southwest, particularly in California. It is the first species of plant in this country found to contain anabasine as the principal alkaloid. A study of certain other species of *Nicotiana* should prove of interest as their alkaloids have not been definitely determined.

Anabasine is a promising contact insecticide,

comparing favorably with nicotine for use against aphids.

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C. R. SMITH

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THE PREPARATION AND PROPERTIES OF BENZENE- d_6

Sir:

We have developed a technique for the exchange reaction between deuterium oxide and benzene, discovered by Horiuti and Polanyi [*Nature*, **134**, 377 (1934); *Trans. Faraday Soc.*, **30**, 1164 (1934)] which permits the ready production of benzene- d_6 . Two cylindrical Pyrex vessels of about 50-cc. capacity are connected by a Pyrex U-tube containing an active nickel catalyst supported on kieselguhr. The catalyst tube is heated externally by a closely fitting electric furnace, and the catalyst reduced (in our case with deuterium) at 420°. After the system is thoroughly evacuated and sealed a sample of 5 cc. of benzene and 10–20 cc. of heavy water is introduced *in vacuo* through a special breakable seal. By means of an electric furnace, which closely fits either cylinder, the water is brought to ebullition and, carrying with it a proportion of benzene vapor, is driven over the catalyst, heated to 200°, where some exchange occurs, the product condensing in the second cylinder appropriately cooled. By reversing the procedure the benzene-water mixture can then be passed once more through the catalyst. Frequent repetition of the process ultimately establishes an equilibrium partition of deuterium between water and benzene. By replacing the hydrogen-diluted deuterium oxide with fresh pure deuterium oxide and continuing the passage over the catalyst, further conversion toward benzene- d_6 can be obtained.

We traced the progress of the exchange by attaching to the reaction system via a quartz-Pyrex seal a cylindrical quartz absorption cell 30 mm. thick. Benzene vapor at room temperatures gives a series of sharply defined ultraviolet absorption bands. Each of the substituted benzenes, C_6H_5D , $C_6H_4D_2$, etc., shows similar bands, displaced toward the ultraviolet by frequency differences varying for each band but roughly constant for each additional D atom. As exchange occurs forming an equilibrium among the 13 benzenes this results in a considerable over-

lapping and complication of the spectrum. With continued progress toward the final state, the overlapping disappears, the sharply defined bands of C_6D_6 only remaining.

In four successive equilibrations with 5 cc. of benzene using an initial 10 cc. of 95% D_2O and then successively 10, 20 and 20 cc. of 100% D_2O a product containing 55, 85, 97 and >99% of the hydrogen as deuterium has been prepared. The deuterium contents have been *estimated* from the absorption spectra. For example, in the 97% product, the bands corresponding to C_6D_5H and C_6D_6 were the only ones visible, the former with about one-fifth the intensity of the latter. Densities of the carefully purified and redistilled samples at the first two stages were, 55%, d^{25}_4 0.9146; 85%, d^{25}_4 0.9349; and the final product had a density of 0.9417. After four separate processes of purification we received approximately 3.5 cc. of final product. Measurements are being made of the Raman spectra, infra-red and ultraviolet absorptions and other physical properties. We are continuing our study of the variables in the preparation and also extending the procedure to other compounds.

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RECEIVED APRIL 22, 1935

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THE HYDROLYSIS OF ERGOTININE AND ERGOCLOAVINE

Sir:

Following our preliminary communications [*J. Biol. Chem.*, **104**, 547 (1934); *THIS JOURNAL*, **57**, 383 (1935); *Science*, **81**, 256 (1935)] regarding the cleavage of ergotinine by alkali to lysergic acid, isobutyrylformic acid, ammonia and a polypeptide which on further hydrolysis with acid yielded proline and phenylalanine, we have made a logical extension of the investigations to the study of the cleavage of ergotinine by acid. Heating with hydrochloric acid resulted in the destruction of the lysergic acid portion of the molecule with the formation of obscure amorphous material. On the other hand, *l*-phenylalanine, $[\alpha]^{20D} -28^\circ$ ($c = 0.39$ in H_2O), was obtained as such while proline was isolated as the methyl ester (*Anal.* C, 55.70; H, 8.81), $[\alpha]^{25D} +33^\circ$ ($c = 0.65$ in CH_3OH), which was further characterized by the gold salt (*Anal.* C, 15.70; H, 2.62; Au, 41.83).