Isobutylation of I with isobutyl bromide gave 65% of ethyl α-carbethoxy-α-cyano-γ-methylpentanoate (II, R = isobutyl), m. p. 120° (calcd. N, 12.38. Found: N, 11.97). Hydrolysis with hydrochloric acid gave 79% of *dl*-leucine, m. p. 278°.

WINTHROP CHEMICAL COMPANY NOEL F. ALBERTSON
RENSSELAER, NEW YORK B. F. TULLAR

RECEIVED FEBRUARY 19, 1945

B-STRAIN AND BASE STRENGTH

Sir:

The peculiar behavior of the methylamines—an increase in base strength from ammonia to methylamine, a further increase to dimethylamine, followed by a marked decrease to trimethylamine—has been ascribed to B-strain.[1]

In the trimethylamine molecule B-strain results from the steric requirements of the three methyl groups crowded about the small nitrogen atom. It is postulated that these requirements are met by a spreading of the C–N–C bond angle to a value greater than the tetrahedral angle. The molecule therefore resists the addition of the acid to the free electron pair which would tend to reduce the bond angle to the tetrahedral value. Trimethylamine thus behaves as a much weaker base than it otherwise would.

Electron diffraction data reveal that the C–P–C bond angle in trimethylphosphine[2] is 100 ± 4°. B-strain must therefore be absent. Consequently, the strength of the phosphine bases should increase regularly with the number of methyl groups: $PH_3 < CH_3PH_2 < (CH_3)_2PH < (CH_3)_3P$.

It is possible to estimate from published data the relative strengths of the phosphine bases. Phosphine does not react with hydrochloric acid. Methylphosphine is absorbed by concentrated hydrochloric acid, but dilution decomposes the salt and liberates the free base. Neither dimethylphosphine nor trimethylphosphine may be liberated from its salts in this way—addition of alkali is necessary.[3] It is thus evident that methylphosphine is a stronger base than phosphine itself, and that both dimethyl- and trimethylphosphine are stronger than the monomethyl derivative. However, no decision can be reached on the critical point—the relative strength of dimethyl- and trimethylphosphine. Accordingly, the hydrochlorides of these two bases were prepared and their relative strength determined.

Dimethylphosphonium chloride is a white crystalline solid of moderate volatility, exhibiting saturation pressures of 1.3 mm. and 46 mm. at 25 and 75° respectively. Trimethylphosphonium chloride is much less volatile. Its saturation pressure is but 0.4 mm. at 75° and 14 mm. at 120°. (Methylphosphonium chloride is an unstable compound of high volatility at room temperature.[3]) The conclusion drawn from these data, that trimethylphosphine is a considerably stronger base than dimethylphosphine, was verified by a competition experiment. Thus, a mixture of 14.0 cc. of each of the two phosphines and of hydrogen chloride yielded 13.9 cc. of uncombined phosphine which analyzed for 95% dimethylphosphine.

Although supplementary data involving other reference acids are desirable and are being procured, it is evident from these data that the strength of the phosphine bases (measured with hydrogen chloride) increases regularly with the number of methyl groups. This verification of prediction is strong support for the B-strain hypothesis. Certainly, no other simple explanation for the markedly different behavior of the methylamines and the methylphosphines is now available.

There is good reason to believe that B-strain is also an important factor in the carbon compounds and can account for many of the peculiar reactions of tertiary butyl and related highly branched derivatives. This point will be developed in subsequent publications.

The assistance afforded by two grants from the Penrose Fund of the American Philosophical Society is gratefully acknowledged.

DEPARTMENT OF CHEMISTRY
WAYNE UNIVERSITY
DETROIT 1, MICHIGAN HERBERT C. BROWN

RECEIVED FEBRUARY 1, 1945

(1) Brown, Bartholomay and Taylor, THIS JOURNAL, **66**, 435 (1944).

(2) Springall and Brockway, *ibid.*, **60**, 996 (1938).

(3) Hofmann, *Ber.*, **4**, 604 (1871).

ON THE BIOGENESIS OF NORNICOTINE AND ANABASINE[1]

Sir:

The localization of the nicotine synthetic mechanism in the root of the tobacco plant (*Nicotiana tabacum*) has been established earlier by the use of reciprocal grafts and of sterile excised root cultures.[2] Similar experiments recently performed in this Laboratory have shown that nornicotine in *Nicotiana glutinosa* and in *N. glauca* is formed only in the leaves and at the expense of nicotine translocated from the roots.

Specifically, it has been found that *N. glutinosa* leaves do not carry out total alkaloid synthesis, for these leaves contain none of the three major tobacco alkaloids when grown on tomato roots. Conversely, *N. glutinosa* roots produce not nornicotine but nicotine, for only nicotine is present in tomato shoots grown on *N. glutinosa* roots. In this respect the root systems of *N. tabacum* and *N. glutinosa* are equivalent and have been experimentally interchanged without resulting marked changes in the alkaloid composition of the leaves. It is concluded, therefore, that the leaves of *N. glutinosa* contain a mechanism capable of convert-

(1) This work was supported in part by the Rockefeller Foundation.

(2) Dawson, *Am. J. Botany*, **29**, 66 (1942); **29**, 813 (1942).

ing nicotine to nornicotine probably by transmethylation.

Nicotiana glauca contains principally anabasine. When grafted to *N. tabacum* roots[3] or when hybridized with the latter species[4] the leaves have been reported to contain predominantly anabasine. Repetition of these experiments in this laboratory has disclosed that the supposed anabasine of the grafts and of the hybrids is actually a mixture of anabasine and nornicotine with usually more nornicotine than anabasine. The difficult separation of anabasine from nornicotine in mixtures of the two was accomplished by repeated fractional crystallizations of the picrates and of the methylated picrates after removal of nicotine by the method of Smith and Smith.[4] To show that the nornicotine present in the leaves of these plants actually arose *in situ* and at the expense of nicotine translocated from the roots, *N. glauca* scions were grafted to *N. tabacum* roots. After a period of growth, a tomato scion was grafted to the apex of each *N. glauca* scion. Ultimately, these three-tiered plants were examined for alkaloids. The *N. glauca* scions contained one part of nicotine to fifty parts of mixed anabasine and nornicotine, while the tomato scions contained only nicotine.

It is now clear that the replacement of the methyl group of nicotine in the plant leaf by the hydrogen atom of nornicotine accounts for the increase in secondary amine content (previously attributed to anabasine[4]) of such graft combinations and genetical hybrids. It follows that expectations[4] of the development of hybrids between *N. tabacum* and *N. glauca* that would be suitable for the commercial extraction of anabasine are without justification.

(3) Schmuck, Kostoff and Borozdina, *Compt. rend. acad. sci. U. R. S. S. (Doklady)*, **25**, 477 (1939).

(4) Smith and Smith, *J. Agr. Research*, **65**, 347 (1942).

BIOLOGY DEPARTMENT
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY RAY F. DAWSON

RECEIVED FEBRUARY 7, 1945

RESOLUTION OF 9-HYDROXYFLUORENE-2-CARBOXYLIC ACID

Sir:

The question whether fluorene has a folded or planar structure is a subject of controversy.[1] It might be thought that the classical methods of stereochemistry should furnish an answer but their application has been precluded by the inability to resolve fluorene compounds containing a 9-asymmetric carbon atom.[2]

We have now succeeded in resolving 9-hydroxyfluorene-2-carboxylic acid into its dextro and levo isomers.

(1) Rieveschl and Ray, *Chem. Rev.*, **23**, 378 (1938).

(2) Bennett and Noyes, *Rec. trav. chim.*, **48**, 895 (1929); THIS JOURNAL, **52**, 3437 (1930); Bapler, Thesis, Ludwig Maximilian University of Munich, pub. Vienna, 1926.

To 11.3 g. of 9-hydroxyfluorene-2-carboxylic acid (m. p. 240°) in 125 cc. of 95% ethanol was added 16.7 g. of strychnine in 125 cc. of chloroform. The resulting solution was distilled to remove the greater part of the chloroform. It was then filtered and placed in a pan of hot water and the whole allowed to come to room temperature. The following morning crystals in the form of rosets, weighing 13.2 g., were obtained. These, recrystallized from 700 cc. of ethanol, sintered at 190° and melted at 203°. This strychnine salt was dissolved in a mixture of 100 cc. of ethanol and 200 cc. of 1% sodium hydroxide. This was poured into a liter of water containing 20 cc. of 6 *N* hydrochloric acid. The white fluffy precipitate was recrystallized from 60 cc. of ethanol and fine needles melting at 263° (block) were obtained.

Anal. Calcd. for $C_{14}H_{10}O_3$: mol. wt., 226. Found: mol. wt. (pinene dibromide), 237; equivalent weight, 226.

These had the following rotations for red, yellow and green light for a solution of 0.7000 g. in 50 cc. of ethanol in a 2-dm. tube: $\alpha^{27}_{656.3}$ +0.82°; $\alpha^{27}_{589.3}$ +1.11°; $\alpha^{27}_{546.3}$ +1.39°; $[\alpha]^{27}_{656.3}$ +21.3°; $[\alpha]^{27}_{589.3}$ +39.6°; $[\alpha]^{27}_{546.3}$ +49.6°.

The levo isomer was isolated similarly. It melted at 260° (block). A solution of 0.7500 g. in 50 cc. of ethanol in a 2-dm. tube gave: $\alpha^{27}_{656.3}$ −0.83°; $\alpha^{27}_{589.3}$ −1.09°; $\alpha^{27}_{546.3}$ −1.35°; $[\alpha]^{27}_{656.3}$ −27.6°; $[\alpha]^{27}_{589.3}$ −36.3°; $[\alpha]^{27}_{546.3}$ −45.0°.

DEPARTMENT OF CHEMISTRY FRANCIS EARL RAY
UNIVERSITY OF CINCINNATI
CINCINNATI 21, OHIO ELIZABETH KREISER

RECEIVED FEBRUARY 10, 1945

INTRODUCTION OF THE ANGULAR METHYL GROUP

Sir:

In a previous report[1] we described the preparation of *cis*- and *trans*-9-methyldecalone-1, using Koebner and Robinson's excellent method for directing the alkylation to the angular position,[2] complemented by a scheme for removal of the protective arylidene group. Although this affords a good source of these particular ketones, there are, as recently pointed out by Birch and Robinson,[3] certain objections to our method from the point of view of more general applicability. We have been engaged for some time in a search for another protective group more easily removed than the arylidene group, and are reporting some of our findings now, because of the appearance of work along somewhat similar lines recently announced by the English workers.[3]

The condensation of decalone-1 with ethyl formate according to a previously described procedure[4] gave excellent yields of the colorless

(1) Johnson, THIS JOURNAL, **65**, 1317 (1943).

(2) Koebner and Robinson, *J. Chem. Soc.*, 566 (1938).

(3) Birch and Robinson, *ibid.*, 501 (1944).

(4) See the preparation of 2-formyl-3-methoxyhydrindone-4 Johnson, Anderson and Shelberg, THIS JOURNAL, **66**, 218 (1944).