synthesized by inversion of an altrose-2-mesylate and will be the subject of a future paper.

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RECEIVED JUNE 24, 1953

2,6-DI-BUTYLPYRIDINE—AN UNUSUAL PYRIDINE BASE

Sir:

2,6-Di-*t*-butylpyridine was synthesized by the reaction of *t*-butyllithium with 2-*t*-butylpyridine.

Excess *t*-butyllithium, prepared from 0.5 mole of *t*-butyl chloride and 1.0 mole of lithium sand in ethyl ether, was added to 0.2 mole of 2-*t*-butylpyridine in 200 ml. of purified 90–100° petroleum ether. The reactants were maintained at −78° for several hours. The temperature was then raised and solvent removed by distillation until the mixture refluxed at 70°. After seven hours, the mixture was hydrolyzed and the base recovered by distillation. The yield was 18.8 g. (0.099 mole) of 2,6-di-*t*-butylpyridine (b.p. 100–101° at 23 mm., n^{20}D 1.5733).

Anal. Calcd. for $C_{13}H_{21}N$: C, 81.6; H, 11.0; N, 7.3. Found: C, 81.4; H, 10.9; N, 7.5.

The picrate could not be prepared. The chloroaurate melted at 184.2–184.5.

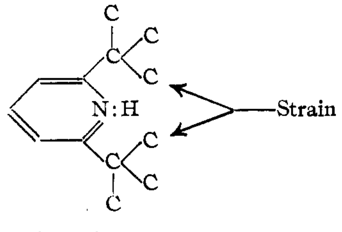
Anal. Calcd. for $C_{13}H_{22}NAuCl_4$: C, 29.4; Au, 37.1. Found: C, 29.7; Au, 36.9.

The base reacts with hydrogen chloride. However, it does not react with methyl iodide or with boron trifluoride. The base thereby permits the quantitative separation of hydrogen chloride from a mixture containing boron trifluoride. For the first time we have a simple method of distinguishing between protonic and Lewis acids.

2,6-Di-*t*-butylpyridine is a relatively weak pyridine base. The pK_a values, measured in 50% aqueous ethanol at 25°, for this and related compounds are

R	Pyridine	2-RC_5H_4N	2,6-$R_2C_5H_3N$
Methyl	4.38	5.05	5.77
Isopropyl	4.38	4.82	5.34
t-Butyl	4.38	4.68	3.58

Thus, 2,6-di-*t*-butylpyridine is weaker than expected by 1.4 pK_a units. We attribute the low pK_a value to steric strain involving the bound proton. The result suggests that the steric requirements of the lone pair on the nitrogen atom must be less than those of the hydrogen atom and its bonding pair.



It follows that the homomorphic molecule, *m*-di-*t*-butylbenzene, should also be strained. This proposal of steric interaction operating between large bulky groups with meta orientation appears capable of accounting for a considerable number of otherwise anomalous data in the literature.

In contrast to other pyridine bases, 2,6-di-*t*-butylpyridine undergoes ready nuclear sulfonation by sulfur trioxide. Identical solutions of sulfur trioxide in liquid sulfur dioxide were prepared. To the solutions (−10°) were added equimolar amounts of pyridine, 2,6-lutidine and 2,6-di-*t*-butylpyridine. After four hours, the solvent was evaporated and the products recovered. Pyridine and 2,6-lutidine formed the sulfur trioxide addition compounds, whereas the 2,6-di-*t*-butylpyridine formed a sulfonic acid, m.p. (dec.) 310°.

Anal. Calcd. for $C_{13}H_{21}NSO_3$: C, 57.6; H, 7.8; N, 5.2. Found: C, 57.5; H, 7.8; N, 5.1.

The S-benzylthiouronium derivative melted at 216.0–216.5°.

Anal. Calcd. for $C_{21}H_{31}N_3S_2O_3$: N, 9.6. Found: N, 9.6.

The product is presumably the 4-sulfonic acid. We are presently attempting to confirm the structure by an independent synthesis. This ready substitution of a pyridine base must result from the blocking of the nitrogen atom. With coördination impossible, the electrophilic reagent readily attacks the heterocyclic nucleus. The result supports the conclusion that the inertness of pyridine rings results primarily from interaction of electrophilic reagent with the lone pair and not from any unusual inertness of the pyridine nucleus.

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RECEIVED JUNE 12, 1953

THE STRUCTURE OF CHAMAZULENE

Sir:

It has been previously reported that the blue essential oil obtained by steam distillation of *Artemisia absorescens* L. contains an azulene.[1,2] This azulene has now been identified as chamazulene by means of its derivatives (trinitrobenzene complex, m.p. 132°, the melting point was not depressed on admixture with an authentic sample; picrate, m.p. 116°) and its infrared spectrum.

The structure of chamazulene, the azulene from camomile oil,[3] has not as yet been established, but from the spectral measurements of Plattner[4] it has been generally assumed to be 1,5-dimethyl-8-isopropylazulene.[5] During the course of this investigation it has been possible to prove its structure as 1,4-dimethyl-7-ethylazulene.

From the acetone cold extract of the above-mentioned plant a crystalline substance was isolated, the analysis of which corresponded to the formula $C_{15}H_{20}O_3$, m.p. 145°, $[\alpha]^{20}$D +63° ($CHCl_3$) (*c* 4.24) (*Anal.* Calcd.: C, 72.7; H, 8.1. Found: C, 72.8; H, 8.2).

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(1) G. Pellini, *Ann. chim. appl.*, **13**, 97 (1923); *Chem. Zentr.*, **94**, IV, 607 (1923).

(2) A. Weizmann, *Bull. Research Council Israel*, **1**, 92 (1952).

(3) L. Ruzicka and A. J. Haagen-Smit, *Helv. Chim. Acta*, **14**, 1104 (1931).

(4) Pl. A. Plattner, *ibid.*, **24**, 283E (1941).

(5) L. H. Chopard-dit-Jean and E. Heilbronner, *ibid.*, **35**, 2187 (1952).