sorbed was 68.4 cc., corresponding to an atom ratio, H/Ni, of 0.0886.

The change of magnetization as measured at room temperature is a rough measure of the change in saturation moment at absolute zero, and hence of the fractional change in unpaired, *d*-band electrons. If nickel metal has 0.6 unpaired electron per atom, then the adsorption of hydrogen caused the addition of approximately 0.068 electron per nickel atom.

At the end of the run the sample was evacuated, with rapid desorption of about one-third of the hydrogen and recovery of two-thirds of the magnetization.

If the hydrogen is first admitted to the sample slowly, rather than flushed on, the chemisorption is isothermal, with no excess diminution of magnetization. If a sample, once exposed to hydrogen, is evacuated at room temperature for an hour, then exposed to hydrogen again, the magnetization falls sharply but no thermal effect occurs.

This method provides a continuous record of electron density in the *d*-band of a functioning nickel catalyst, under widely varying conditions of pressure and temperature. The method also applies to any other gas capable of being chemisorbed on nickel, and to reactions, such as oxidation or reduction, under conditions identical with those encountered in actual catalytic practice.

The writer is indebted to Dr. L. N. Mulay and Mr. Edward L. Lee who first observed the thermal effect in this laboratory on other apparatus.

This work was supported by the Office of Naval Research.

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY P. W. SELWOOD
EVANSTON, ILLINOIS

RECEIVED NOVEMBER 22, 1955

THE TOTAL SYNTHESIS OF *dl*-DEHYDROABIETIC ACID

Sir:

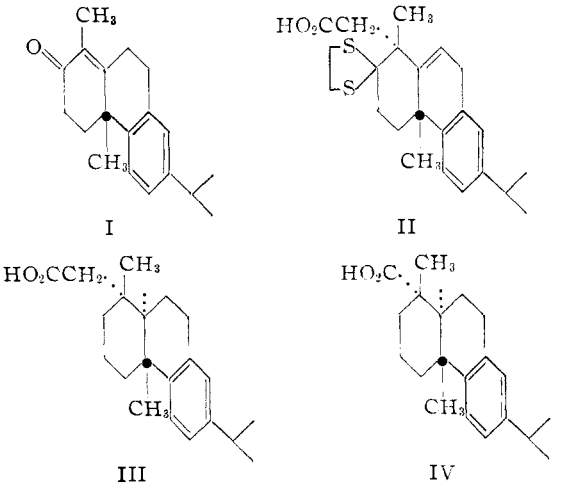
We would like to report the total synthesis of *dl*-dehydroabietic acid,[1] the first synthesis of a diterpenoid resin acid.

2-Isopropylnaphthalene[2] was sulfonated to the 6-sulfonic acid, isolated as its *sodium salt* (found: C, 57.3; H, 4.7); **sulfonamide,** m.p. 190–190.5° (found: C, 62.4; H, 5.9) which was transformed into **6-isopropyl-2-naphthol,** m.p. 111.5–112.5° (found: C, 83.8; H, 7.8), by fusion with potassium hydroxide. The structure of the naphthol was proved by independent synthesis of its **methyl ether,** m.p. 63.5–64.5° (found: C, 84.0; H, 8.1), from 6-methoxy-2-acetonaphthone[3] by reaction with ethyl chloroacetate in the presence of potassium *t*-butoxide to produce the **glycidic ester,** m.p. 107–108.5° (found: C, 71.4; H, 6.4), which was hydrolyzed and decarboxylated to α-methyl-6-methoxy-2-naphthaleneacetaldehyde; **semicarbazone,** m.p. 173–174.5° (found: C, 66.3; H, 6.2). Wolff–Kishner reduction of the aldehyde gave 2-isopropyl-6-methoxynaphthalene, identical with the product described above.

Reduction of 6-isopropyl-2-naphthol with sodium in liquid ammonia[4] gave 6-isopropyl-2-tetralone, b.p. 123–126° (0.6 mm.); ***p*-nitrophenylhydrazone,** m.p. 172.5–174.5° (found: C, 70.9; H, 6.7; N, 13.0). Monomethylation of this β-tetralone could be achieved satisfactorily only by the reaction of its pyrrolidine enamine with methyl iodide[5] to yield 6-isopropyl-1-methyl-2-tetralone, b.p. 120–123° (0.6 mm.); **2,4-dinitrophenylhydrazone,** m.p. 142.5–144° (found: C, 63.1; H, 5.8; N, 14.5).

Condensation with 1-diethylamino-3-pentanone methiodide[6] or ethyl vinyl ketone gave 4,4a,9,10-tetrahydro - 1,4a - dimethyl - 7 - isopropyl - 2(3H)-phenanthrone (I), b.p. 160–168° (0.25 mm.), λ_{max}^{alc} 245 mμ, ε 15,000; **2,4-dinitrophenylhydrazone,** m.p. 173.5–175° (found: C, 67.0; H, 6.3; N, 12.6). Alkylation of the α,β-unsaturated ketone with ethyl bromoacetate,[7] followed by thioketal formation with ethanedithiol and base hydrolysis gave **1,2,3,4,4a,9-hexahydro-1,4a-dimethyl-2-ethylenedithio - 7 - isopropyl - 1 - phenanthreneacetic acid** (II), m.p. 183–186° (found: C, 68.3; H, 7.5) as the only isolatable crystalline isomer. Transformation into the methyl ester, followed by Raney nickel desulfurization, hydrolysis, and hydrogenation with palladium-charcoal in acetic acid afforded **1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-isopropyl-1-phenanthreneacetic acid** (III), (*dl*-homodehydroabietic acid), m.p. 173–174° (found: C, 80.3; H, 9.4). The identity of the infrared spectrum of the synthetic acid with that of the **homoacid,** m.p. 146–147.5° (found: C, 80.4; H, 9.7) prepared by Arndt–Eistert homologation of *d*-dehydroabietic acid served to confirm its anticipated structure and stereochemistry.

Barbier–Wieland degradation of the synthetic homoacid *via* the diphenylcarbinol and diphenylethylene gave *dl*-**dehydroabietic acid** (IV), m.p. 179.5–180.5° (found: C, 80.3; H, 9.3). The in-



(1) The most recent experiments in this field are described by W. E. Parham, E. L. Wheeler and R. M. Dodson, THIS JOURNAL, **77,** 1166 (1955).

(2) F. Bergmann and A. Weizmann, *J. Org. Chem.*, **9,** 352 (1944).

(3) R. Robinson and H. N. Rydon, *J. Chem. Soc.*, 1934 (1939).

(4) *Cf.* A. J. Birch, *ibid.*, 430 (1944).

(5) G. Stork, R. Terrell and J. Szmuszkovicz, THIS JOURNAL, **76,** 2029 (1954).

(6) *Cf.* J. W. Cornforth and R. Robinson, *J. Chem. Soc.*, 1855 (1949).

(7) *Cf.* J. M. Conia, *Bull. soc. chim.*, 690; 943 (1954), for a discussion of related reactions.

frared spectrum of the synthetic acid was identical with that of *d*-dehydroabietic acid, m.p. 171°, from natural sources.

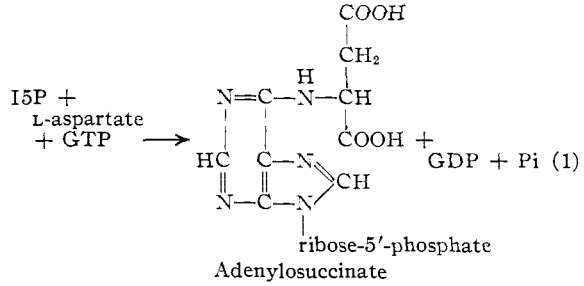
CHANDLER LABORATORY
COLUMBIA UNIVERSITY GILBERT STORK
NEW YORK 27, NEW YORK JOHN W. SCHULENBERG

RECEIVED DECEMBER 10, 1955

INVOLVEMENT OF GUANOSINE TRIPHOSPHATE IN THE SYNTHESIS OF ADENYLOSUCCINATE FROM INOSINE-5′-PHOSPHATE[1]

Sir:

Our studies on the amination of a pyrimidine nucleotide[2] led us to an investigation of the amination of a purine nucleotide to determine whether the reactions are similar. With an enzyme purified about 40-fold from extracts of *Escherichia coli* B, evidence now has been obtained for the synthesis of adenylosuccinate, a compound first prepared and characterized by Carter and Cohen,[3] from I5P[4] and L-aspartate in a reaction involving GTP, as illustrated in equation (1). Adenylosuccinate



Adenylosuccinate

isolated from reaction (1) was cleaved by an extract of *E. coli* B to yield A5P (equation (2)), a reaction first described by Carter and Cohen[3] with an enzyme from yeast.

$$\text{Adenylosuccinate} \longrightarrow \text{A5P} + (\text{fumarate}) \quad (2)$$

With the partially purified enzyme preparation A5P, guanosine-5′-phosphate, GDP, and the di- and triphosphates of adenosine, cytidine, uridine, and inosine were incapable of replacing GTP. L-Asparagine, D-aspartate, L-glutamate, and L-glutamine could not substitute for L-aspartate (each 7×10^{-4} *M*). D-Aspartate did not inhibit the synthesis of adenylosuccinate.

The stoichiometry of the reaction was studied with the partially purified enzyme (Table I). I5P was identified by its absorption spectrum (peak at 249 mμ, λ250/λ260 = 1.60, λ280/λ260 = 0.21, at *p*H 2), GDP and GTP by their absorption spectra (peaks at 256 mμ, λ250/λ260 = 0.99, λ280/λ260 = 0.68, at *p*H 2), and by their molar ratios of guanine, pentose, acid-labile P, and total P of 1.00:1.02:1.02:2.01, and 1.00:0.94:1.94:2.90, respectively. Adenylosuccinate was identified by its absorption spectrum[3] (peak at 267 mμ, λ250/λ260 = 0.64, λ280/λ260 = 0.68, at *p*H 2; peak at 269 mμ, λ250/λ260 = 0.60, λ280/λ260 = 0.81, at *p*H 12). Further, when L-aspartate labeled with C^{14} in both carboxyl groups was used as a substrate, as shown in the table, it was incorporated into adenylosuccinate without dilution. Likewise, in an experiment with 8-C^{14}-labeled I5P (37,200 c.p.m./μmole), the specific activity of the adenylosuccinate (36,600 c.p.m./μmole) was the same as the substrate. Using the molar extinction coefficient found by Carter and Cohen[3] (E_M 267 mμ at *p*H 1 = 16.9×10^3), the product yielded molar ratios of pentose and total P of 0.99 and 0.96, respectively. No Pi was liberated during incubation in 1 *N* H_2SO_4 in a boiling water-bath for 15 minutes, but from 0.107 μmole of product, 0.109 μmole of Pi was released by 5′-nucleotidase.[5] No detectable diazotizable amine reaction[6] occurred with the product. Incubation of the product, with an extract of *E. coli* B, yielded a radioactive compound (88% of the counts) whose anion-exchange chromatographic behavior was indistinguishable from that of authentic A5P.

TABLE I

STOICHIOMETRY OF ADENYLOSUCCINATE SYNTHESIS

The reaction mixture (29.4 ml.) contained 4.2 ml. of glycine buffer (1 *M*, *p*H 8.0), 1.68 ml. of $MgCl_2$ (0.1 *M*), 1.68 ml. of C^{14}-carboxyl-labeled-L-aspartate (0.01 *M*, 147,000 c.p.m./μmole), 0.85 ml. of I5P (0.01 *M*), 1.42 ml. of GTP (0.0059 *M*), and 4.2 ml. of the enzyme preparation (containing 1.85 mg. of protein). An aliquot of the reaction mixture (15 ml.) was placed immediately in a boiling water-bath for 2.5 minutes, the remainder was incubated at 37° for 50 minutes, and then heated for 2.5 minutes in a boiling water-bath.

	0 min. μmoles	50 min. μmoles	μmoles	Δ Total c.p.m.	Specific activity c.p.m./μmole
I5P[a,b]	3.43	1.75	−1.68	0	
GTP[c]	3.39	1.63	−1.76	0	
L-Aspartate[d]	6.87	5.21	−1.66	−244,020	147,000
Adenylosuccinate[e]	0.00	1.61 (1.66)[g]	+1.61 (+1.66)	+227,180	141,100
GDP[c]	0.00	1.72	+1.72	0	
Pi[f]	0.39	2.08	+1.69		

[a] Anion-exchange chromatography of aliquots of the reaction mixtures (12 ml.) gave complete separations of aspartic acid and each of the nucleotides. [b] Estimated spectrophotometrically at 250 mμ. [c] Estimated spectrophotometrically at 260 mμ. [d] Estimated by radioactivity measurements. [e] Estimated spectrophotometrically at 267 mμ. [f] Estimated by the method of C. H. Fiske and Y. SubbaRow, *J. Biol. Chem.*, **66**, 375 (1925), before chromatography. [g] Values in parentheses were determined by optical density measurements at 280 mμ before chromatography.

This work, in progress at the time Abrams and Bentley[7] reported on the conversion of I5P to adenosine-5-phosphate with rabbit bone marrow extracts, is in agreement with their results.

The author is indebted to W. H. Eto for valuable technical assistance.

DEPARTMENT OF MICROBIOLOGY
WASHINGTON UNIVERSITY SCHOOL OF MEDICINE
ST. LOUIS 10, MISSOURI IRVING LIEBERMAN

RECEIVED NOVEMBER 28, 1955

(1) This investigation was supported by a grant from the National Institutes of Health, Public Health Service.

(2) I. Lieberman, THIS JOURNAL, **77**, 2661 (1955).

(3) C. E. Carter and L. H. Cohen, *ibid.*, **77**, 499 (1955).

(4) Abbreviations used: Inosine-5′-phosphate, I5P; adenosine-5′-phosphate, A5P; guanosine diphosphate, GDP; guanosine triphosphate, GTP; Inorganic orthophosphate, Pi.

(5) L. A. Heppel and R. J. Hilmoe, *J. Biol. Chem.* **188**, 665 (1951).

(6) J. M. Ravel, R. E. Eakin and W. Shive, *ibid.*, **172**, 67 (1948).

(7) R. Abrams and M. Bentley, THIS JOURNAL, **77**, 4179 (1955).