

Dimethylamino *t*-butylborane and methylamino *t*-butylborane were prepared in an identical fashion except that the gaseous amines were passed through the reaction mixture with a gas inlet tube. In these cases excess amine was employed and the completion of the reaction was indicated by the cessation of hydrogen evolution.

^{B11} N.m.r. Spectra.—A Varian high resolution nuclear magnetic resonance spectrometer was employed at 12.8 mc. Spectra were obtained with pure liquids and measured relative to trimethyl borate contained in a capillary tube inserted in the sample tube.

Molecular Weight Determinations.—Solutions of bis-(diethylamino) *n*-butylborane, diethylamino *t*-butylborane and methylamino *t*-butylborane were prepared with pure benzene solvent in a glove-box. A completely sealed and

dried freezing point depression apparatus was employed with a Beckmann thermometer in the usual manner. Determinations were carried out in duplicate. The observed molecular weights were: bis-(diethylamino) *n*-butylborane, 202 and 198 (theor. 212); diethylamino *t*-butylborane, 143 and 151 (theor. 141); and methylamino *t*-butylborane, 198 and 195 (theor. 99).

Acknowledgment.—The author is indebted to Mrs. Carolyn P. Haney for the nuclear magnetic resonance measurements. This work was carried out under the sponsorship of the U. S. Army Ordnance Corps, Contract No. DA-01-021-11878.

[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALA.]

The Nature of the Colored 6,9-Bis-pyridine Decaborane Molecule, B₁₀H₁₂Py₂

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RECEIVED FEBRUARY 6, 1961

Several highly colored 6,9-bis-pyridine decaborane derivatives have been prepared from substituted pyridines and their ultraviolet and visible absorption spectra determined. The absorption band found at longest wave length was successfully correlated with the Hammett σ -constant characteristic of each substituent. Electron-withdrawing substituents such as the *p*-cyano group markedly reduce the transition energy associated with this absorption band. Evidence is presented which indicates that the π -electron system of the pyridine nucleus is extended well into the B₁₀H₁₂ fragment.

The reaction of pyridines with decaborane has recently been examined by many workers.²⁻⁵ Due to the highly colored nature of these materials, other investigators^{6,7} have employed their quantitative formation as the basis of a colorimetric method for the determination of decaborane. The method of synthesis (*vide infra*), analyses and other data support the conclusion that these materials are actually members of the B₁₀H₁₂X₂ family.⁸ Reddy and Lipscomb⁹ have recently reported the structure of the bis-acetonitrile product, B₁₀H₁₂(CH₃CN)₂, and have discussed its bonding in terms of the three-center bond topology of Dickerson and Lipscomb.^{10,11} More recently, Sands and Zalkin¹² have determined the structure of the bis-dimethyl sulfide derivative, B₁₀H₁₂[S(CH₃)₂]₂. The structure of this compound was found to be in excellent agreement with that of the bis-acetonitrile product.⁹

Quite a large number of B₁₀H₁₂X₂ compounds have been prepared and characterized in the past. The ligand, X, has been varied widely and encom-

passes such species as phosphines,⁸ dialkylcyanamides,⁸ amines,¹³ nitrile,¹⁴ isonitriles,¹⁵ phosphite esters¹⁶ and tetrazoles.¹⁶ The pure B₁₀H₁₂X₂ compounds have been observed to be colorless when X does not have an extended π -electron system. The fact that the corresponding pyridine derivatives, B₁₀H₁₂Py₂, were highly colored and diamagnetic suggested an unusual electronic interaction of the B₁₀H₁₂ unit and the bonded pyridine molecule. In this paper we report the synthesis of several symmetrical 6,9-bis-pyridine decaboranes which bear substituents on the pyridine rings and a correlation of their spectroscopic properties with Hammett σ -constant characteristic of those substituent groups. Lastly, these results are combined in a rationale which makes use of the known structural features of B₁₀H₁₂X₂ molecules^{9,12} and the topological treatment of Lipscomb.^{10,11}

Results and Discussion

The synthesis of the required symmetrically substituted¹⁷ 6,9-bis-pyridine decaborane derivatives was accomplished in two steps. The 6,9-bis-diethyl sulfide intermediate was employed since the structure of the corresponding dimethyl sulfide derivative is known¹² and the displacement of diethyl sulfide by substituted pyridines occurs with great ease at room temperature and *without* hydrogen evolution.¹⁸ The preparation of 6,9-bis-diethyl sulfide decaborane from diethyl sulfide and decaborane may be accomplished in 83% yield and the subsequent step is always very effi-

(1) Visiting Lecturer, Harvard University, Fall, 1960.

(2) W. A. Mosher, H. C. Beachell, *et al.*, Univ. of Delaware, Newark, Del., Contract No. DA-36-034-ORD-2526-RD (unclassified), Quarterly Report Nos. 1-5, "Adducts of Boron Compounds."

(3) H. C. Beachell, D. E. Hoffman and B. F. Dietrich, *Angew. Chem.*, **72**, 40 (1960).

(4) L. A. Burkardt and N. R. Fetter, Abstracts of Papers, 135th Meeting, American Chemical Society, Boston, Mass., p. 45-M.

(5) L. A. Burkardt and N. R. Fetter, *Chemistry & Industry*, **38**, 1191 (1959).

(6) W. H. Hill and M. S. Johnston, *Anal. Chem.*, **27**, 1300 (1955).

(7) D. L. Hill, E. I. Gipson and J. F. Hancock, *ibid.*, **28**, 133 (1956).

(8) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **80**, 6685 (1958), report several examples.

(9) J. Van der Maas Reddy and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 610 (1959).

(10) R. E. Dickerson and W. N. Lipscomb, *ibid.*, **27**, 212 (1957).

(11) For a summary of this topological method see W. N. Lipscomb, "Advances in Inorganic and Radiochemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1959.

(12) D. E. Sand and A. Zalkin, Abstracts of Papers, International Congress of Crystallography, 1960.

(13) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5519 (1959).

(14) R. Schaefer, *ibid.*, **79**, 1006 (1957).

(15) B. M. Graybill and M. E. Hawthorne, unpublished results.

(16) N. R. Fetter, *Chemistry & Industry*, 1548 (1959).

(17) Unsymmetrical derivatives, B₁₀H₁₂XX', have recently been prepared and will be reported in the near future.

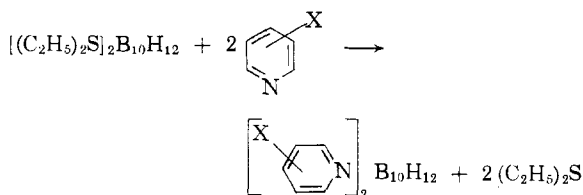
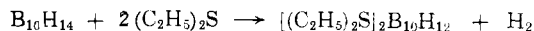
(18) For previous examples of similar displacement reactions see M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **80**, 6685 (1958).

TABLE I
 SUBSTITUTED 6,9-BIS-PYRIDINE DECABORANE COMPOUNDS

X in $\left(\text{X}-\text{C}_5\text{H}_4\text{N}\right)_2$	$\text{B}_{10}\text{H}_{12}$	Dec. Pt., °C.	Yield, %	Analyses, %							
				B	C	H	N	B	Found ^a C	H	N
<i>p</i> -OCH ₃		>275	97	31.99	42.58	7.69	8.27	30.65	40.25	7.23	6.47
<i>p</i> -CH ₃		262	91	35.34	47.03	8.49	9.14	35.86	46.01	8.37	8.76
H		247	82	38.89	43.13	7.91	10.06	38.19	44.10	7.96	9.68
<i>p</i> -Cl		>275	97	31.17	34.57	5.76	8.07	32.79	34.41	6.98	8.49
<i>p</i> -Br		>275	78	24.87	27.59	4.60	6.44	24.72	27.44	5.06	6.21
<i>m</i> -Cl		233	86	31.17	34.57	5.76	8.07	30.69	34.40	6.01	8.31
<i>p</i> -CH ₃ CO ^b		>275	86	29.87	46.38	7.18	7.73	28.94	43.34	7.34	8.41
<i>p</i> -CN		>275	85	32.97	43.88	6.09	17.06	33.04	43.53	6.12	16.57
2,3-Benzo-(quinoline)		243	92	28.61	57.11	6.87	7.40	27.11	55.75	6.90	7.72

^a Difficulty was encountered in analysis due to incomplete combustion and formation of boron carbide. Very high temperatures are required to obtain reasonable results. ^b Purification of this material by recrystallization from acetonitrile resulted in some reduction of the carbonyl group as evidenced by its infrared spectrum which showed a strong carbonyl absorption at 5.9 μ along with a weak OH band at 3.05 μ .

cient. Table I presents the yield and characterization data obtained.



The unsubstituted 6,9-bis-pyridine decaborane was also prepared directly from pyridine and decaborane as previously described.² A tris-complex between decaborane and pyridine has also been reported.⁴ Recrystallization of the bis-adduct yielded crystals whose infrared spectrum was identical to that of the same material prepared as outlined above.

The substituted 6,9-bis-pyridine derivatives obtained lacked great solubility in organic solvents. However, recrystallization of the reaction products was accomplished from acetonitrile. In all cases save one, the products were of good crystal habit when viewed under the microscope.

Recrystallization of the 6,9-bis-*p*-acetylpyridine decaborane from acetonitrile apparently resulted in a small amount of reduction of the *p*-acetyl group. Evidence for this change was found in the infrared spectrum of the recrystallized product which contained a weak -OH stretching band at 3.05 μ . This minor contaminant could not be removed, but its presence in low concentration should not seriously affect the spectroscopic results reported below.

Due to the low solubility of the 6,9-bis-pyridine decaboranes, all attempts to obtain meaningful B¹¹ n.m.r. spectra were futile. Additional difficulties were encountered during the analyses for carbon, hydrogen and nitrogen (see Table I). In some cases incomplete oxidation occurred during combustion and the results were generally poor. However, the method of synthesis and the analytical results clearly point to the fact that the reported derivatives are the desired 6,9-bis-pyridine decaborane derivatives.

In the infrared region each derivative displayed certain common absorptions and other absorptions

due to the substituent group on pyridine. In all cases B-H stretching was found at 4 μ . No B-H-B bridge stretching bands were observed. The cyano group of the *p*-cyano pyridine derivative absorbed at 4.45 μ while the carbonyl group of the *p*-acetyl derivative absorbed at 5.9 μ . Pyridine ring absorptions were also present in the regions of 6-6.5 μ and 11-14 μ .

In addition to the compounds discussed above, 6-diethylamine-9-pyridine decaborane was available from another study¹⁶ as well as 6,9-bis-triethylamine decaborane previously described.¹³ These materials served as model compounds in the spectroscopic studies described below.

The 6,9-bis-pyridine decaborane derivatives and the model compounds described above were examined in the accessible ultraviolet and visible regions of the spectrum in acetonitrile solvent. Table II presents the relevant data and the values of the Hammett σ -constants chosen for correlation purposes.¹⁹

It will be seen in Table II that each compound examined has at least one short wave length absorption maximum or inflection point. The presence of this band in the 6,9-bis-triethylamine decaborane spectrum indicates that the transitions responsible for these bands are independent of the nature of the attached ligands. The compounds which show only inflections rather than well-defined absorption maxima also exhibited strong end absorption. This end absorption may be a result of $n-\pi$ or $\pi-\pi$ transitions characteristic of the ligand itself.

The less intense absorption maximum present in the spectrum of each of the substituted 6,9-bis-pyridine decaboranes is obviously dependent upon the nature of the attached ligand. As seen in Table II the color of 6,9-bis-pyridine decaborane may be varied from a very pale yellow to a deep red simply by changing the nature of the substituent group on the pyridine ligand. More precisely, a plot of $1/\lambda_{\text{max}}$ versus σ for the corresponding *m*- and *p*-substituent on the pyridine ligand provides the linear relationship shown in Fig. 1. The fact that the linear relationship of excitation energy²⁰

(19) In all cases other than *p*-acetyl and *p*-cyano the usual σ -constant was employed. In the two exceptional cases the σ of H. Jaffé, *Chem. Revs.*, **63**, 191 (1953), were chosen.

(20) The parameter $1/\lambda_{\text{max}}$ is proportional to the frequency of the absorbed radiation and the excitation energy.

TABLE II
ULTRAVIOLET AND VISIBLE SPECTRA OF 6,9-BIS-PYRIDINE
DECARBORANES AND MODEL COMPOUNDS

X in $B_{10}H_{12}$	Color	λ_{max} m μ	Molar extinct. coeff., ϵ $\times 10^{-3}$	σ -Constant for X
p -CH ₃ O	Pale yell.	351	6.68	-0.268
		243	26.00	
p -CH ₃	Yellow	372	4.65	- .170
		237	10.30	
H	Yellow	380	3.92	.00
		241	8.13	
p -Cl	Yell-or.	400	3.56	+ .226
		224	12.00	
p -Br	Yell-or.	398	2.30	+ .232
		239	7.99	
m -Cl	Orange	405	6.76	+ .373
		264	Infl.	
		236	Infl.	
p -CH ₃ CO	Red	460	6.51	+ .870 ^a
		272	Infl.	
		236	Infl.	
p -CN	Red	467	8.21	
		273	11.00	+1.000 ^a
2,3-Benzo	Red-or.	447	4.73	
		302	11.60	
		233	65.70	
o -CH ₃ O	Yellow	380	5.54	
		268	10.40	
o -C ₆ H ₅	Orange	410	2.79	
		255	Infl.	
^b	Yellow	381	3.01	
		245	8.41	
^c	White	244	6.25	

^a σ^- of Jaffé (ref. 19). ^b $PyB_{10}H_{12}NH(C_2H_5)_2$ (ref. 18).
^c $B_{10}H_{12}[N(C_2H_5)_2]_2$ (ref. 13).

and substituent constant exists strongly suggests that the corresponding transition involves the π -electron system of the pyridine ligand. The fact that electron-withdrawing substituents decrease the required excitation energy indicates that the $B_{10}H_{12}$ unit is an *electron-donor in the excited state*.²¹ Such an interaction demands that the $B_{10}H_{12}$ unit possess an orbital of suitable symmetry and configuration for overlap with the π -electron system of the ligand.

The topological representation of $B_{10}H_{12}X_2$ molecules^{9,22} which is in agreement with the observed structures of the 6,9-bis-acetonitrile⁹ and 6,9-bis-dimethyl sulfide¹² decaboranes is presented in Fig. 2. In Fig. 2 pyridine is employed as the ligand and the commonly accepted²³ numbering system of decaborane is employed. The 6- and 9-boron atoms of the $B_{10}H_{12}$ unit are trigonally hybridized with the trigonal plane perpendicular to that of the paper. The remaining p -orbitals of the 6- and 9-boron atoms are involved in open three-center bonds^{10,11} with tetrahedral orbital lobes from the 5-, 7- and 8-, 10-boron atoms, respectively.

(21) This conclusion is based upon the commonly employed assumption that excited states are more strongly influenced by structural changes than are ground state molecules.

(22) W. N. Lipscomb, *J. Inorg. Nucl. Chem.*, **11**, 1 (1959).

(23) This numbering system is the one accepted by the Boron Nomenclature Committee, as described by G. Schaeffer, Abstracts of Papers of the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958, 2-L.

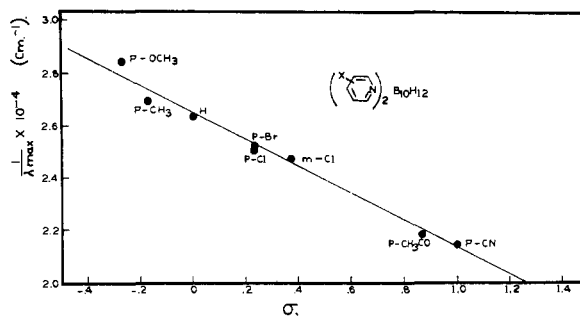


Fig. 1.—Correlation of excitation energies with σ -constants.

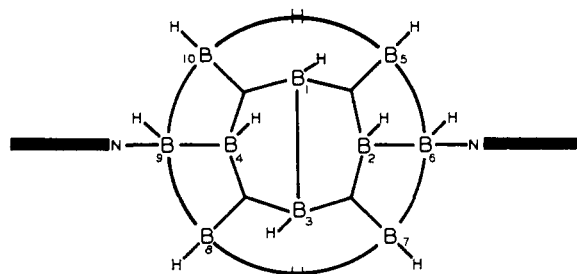


Fig. 2.—A topological representation of the probable valence bond structure of $(pyridine)_2B_{10}H_{12}$ with the pyridine rings in the perpendicular plane.

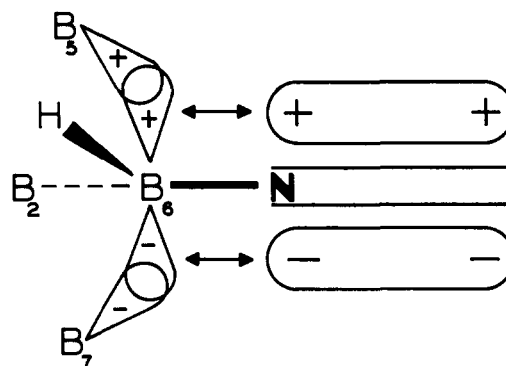
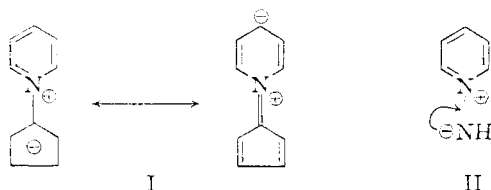


Fig. 3.—Partial structure of $(pyridine)_2B_{10}H_{12}$ showing possible p - π overlap.

If the ligands are rotated in such a fashion as to bring the plane of the pyridine rings into a plane perpendicular to that of the paper, overlap may occur between the open three-center bond and the pyridine π -electron system. This array is presented in Fig. 3, using a localized orbital picture. Thus, it is possible to extend the pyridine molecular orbital system into the $B_{10}H_{12}$ unit. Beyond this point, little may be said at the present time. The transition responsible for the long wave length maxima could conceivably arise from a number of possible excitation processes. The excitation of an electron from a bonding three-center or two-center orbital to an anti-bonding π -orbital which involves the pyridine system appears likely.

Strong experimental evidence against the simultaneous use of both pyridine rings in the excitation process is found in the spectrum of 6-diethylamine-9-pyridine decaborane¹⁸ (see Table I). The spectrum of this material is virtually the same as that of 6,9-bis-pyridine decaborane.

The proposal of back coordination into a pyridine ring is new in the area of boron hydride chemistry. However, several systems common to carbon chemistry apparently exhibit this phenomenon. One excellent example of such an interaction is presented by the red-gold compound I, recently described by Kosower and Ramsay.²⁴



The conjugate base of the N-aminopyridinium ion II is blue-violet²⁵ and constitutes another example of such back coordination.

Experimental

Materials.—Decaborane was sublimed before use. All of the substituted pyridines except the *p*-methoxy derivative were obtained from either Columbia Organic Chemical Co. or Aldrich Chemical Co. and were used without further purification. Both pyridine and quinoline (Eastman Chemical Co.) were distilled before use. Acetonitrile was Eastman Spectrograde.

Preparation of *p*-Methoxypyridine.—The *p*-methoxypyridine was prepared from sodium methoxide and *p*-chloropyridine in essentially the same way as reported for the synthesis of the *o*-isomer.²⁶ The product had a boiling point of 98–100° at 38 mm. pressure and a refractive index of n_D^{25} 1.5184. These compare favorably with the reported constants²⁷ b.p. 102° (40 mm.) and n_D^{25} 1.5176. The infrared

(24) E. M. Kosower and B. G. Ramsey, *J. Am. Chem. Soc.*, **81**, 856 (1959).

(25) Reported by R. Huisgen at the Robert A. Welch Foundation Conference on Molecular Structure and Organic Reactions, Houston, Tex., April, 1960, and suggested to the authors by Prof. R. B. Woodward.

(26) T. B. Grave, *J. Am. Chem. Soc.*, **46**, 1466 (1924).

(27) D. G. Leis and B. C. Curran, *ibid.*, **67**, 79 (1945).

spectrum was also consistent for that expected for *p*-methoxypyridine.

Preparation of 6,9-Bis-diethyl Sulfide Decaborane.—In a 500-cc. round-bottom flask, equipped with condenser, were placed 45 g. of sublimed decaborane (0.34 mole), 100 ml. of dry benzene and 120 ml. of ethyl sulfide. The mixture was refluxed under dry nitrogen for about 3 hours or until no more gas was evolved. The yellow solution was cooled to room temperature and the product crystallized out by adding ether and pentane. After cooling, the fluffy crystals were filtered and washed with ether; m.p. 90–91°. The total yield was 85 g. (83%).

Anal. Calcd. for $B_{10}C_8H_{32}S_2$: B, 36.07; C, 31.98; H, 10.66. Found: B, 34.97; C, 32.43; H, 11.02.

Preparation of 6,9-Bis-pyridine Decaborane Derivatives.—All of the pyridine decaborane derivatives were prepared in the same manner with the various yields and results listed in Table I. The compounds were recrystallized from large volumes of hot acetonitrile. A typical example of the general procedure in these preparations is listed below for the parent compound.

6,9-Bis-pyridine Decaborane.—In 40 ml. of benzene were dissolved 3 g. (0.01 mole) of bis-diethyl sulfide decaborane and 2 g. (0.025 mole) of pyridine. The solution was stirred under an atmosphere of nitrogen at room temperature for about 4 hours. The yellow solid which separated from solution was filtered and dried; yield 2.3 g. (82%). Recrystallization from much acetonitrile afforded small yellow crystals.

Ultraviolet Spectra.—The spectra of the 6,9-bis-pyridine decaborane derivatives were measured with a model DK-1 Beckman spectrophotometer. Samples were weighed out accurately on a micro-balance and diluted with acetonitrile to a 10-ml. volume to give approximately a 10^{-4} M solution.

Infrared Spectra.—A model 137 Perkin-Elmer Infracord was used to obtain Nujol mull infrared spectra of the pyridine derivatives.

Acknowledgments.—The authors wish to thank Mr. R. D. Strahm for the ultraviolet spectra and Mr. J. Sanford for the elemental analyses. We are also indebted to Dr. Hans Jonassen for the magnetic susceptibility measurements which showed these compounds to be diamagnetic. This work was performed under the sponsorship of the U. S. Army Ordnance Corps, Contract No. DA-01-021-ORD-11878.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON 6, WISC.]

Studies on the 4-Hydroxycoumarins. XVII.^{1a} The Resolution and Absolute Configuration of Warfarin^{1b}

BY BRUCE D. WEST, SEYMOUR PREIS, COLLIN H. SCHROEDER AND KARL PAUL LINK

RECEIVED FEBRUARY 9, 1961

The anticoagulant *rac*-warfarin [3-(α -acetylbenzyl)-4-hydroxycoumarin] has been completely resolved through its quinidine and quinine enolates. The levorotatory (in aqueous alkali) form is about seven times more active in the rat than its enantiomer. (–)-Warfarin and (+)(S)- β -phenylcaproic acid have been converted by reactions not involving the asymmetric centers to the two enantiomers of 1,1-di-(*o*-anisyl)-3-phenylhexan-1-ol. The (S) configuration has been assigned to (–)-warfarin.

The anticoagulant *rac*-warfarin [3-(α -(acetylbenzyl)-4-hydroxycoumarin] was synthesized here by the Michael condensation of 4-hydroxycoumarin with benzalacetone.² In 1948, it was proposed for

(1) (a) Previous paper in this series: S. Roseman, C. F. Huebner, R. Pankratz and K. P. Link, *J. Am. Chem. Soc.*, **76**, 1650 (1954). (b) Published with the approval of the Director of the Agricultural Experiment Station. Supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

(2) M. Ikawa, M. A. Stahmann and K. P. Link, *J. Am. Chem. Soc.*, **66**, 902 (1944).

rodent control and rapidly gained world-wide use. In 1952, its water-soluble sodium derivative was introduced for clinical use. It now rivals Dicumarol® [3,3'-methylenebis-(4-hydroxycoumarin)], through which oral anticoagulation was made possible.³

Resolution of *rac*-Warfarin.—Attempts to form covalent diastereoisomers with the resolving agents *l*-menthoxyacetyl chloride,⁴ *l*-menthydrazide⁵ and

(3) K. P. Link, *Circulation*, **19**, 97 (1959).