with 0.08 *N* ammonium hydroxide. Kanamycin B base is soluble in water, slightly soluble in the lower alcohols, insoluble in non-polar organic solvents, and decomposes over a wide range above 170°, $[\alpha]_D^{24}$ +135 (*c* 0.63, H_2O). It gives positive Molisch, Elson–Morgan and ninhydrin tests but gives negative reducing sugar tests and yields no furfural-like material after 40% sulfuric acid treatment at 100° for 100 min., in contrast to kanamycin. The infrared spectrum in KBr shows the following absorption maxima: 2.96, 3.44, 6.35, 6.48 (shoulder), 6.74, 6.85 (shoulder), 7.25, 7.45, 7.86, 8.08, 8.28, 8.76, 9.55, 9.65, 10.4, and 11.15.

Kanamycin B base was recrystallized repeatedly from 90% ethanol and dried to constant weight at 135° under vacuum. *Anal.* C, 44.7, 44.8; H, 7.46, 7.55; N, 12.56, 12.55; neut. eq., 106; mol. wt., 1170 (Rast method with urea as solvent).

Kanamycin B was characterized as a polyacetyl derivative, prepared from kanamycin B by acetic anhydride–pyridine acetylation. Acetylation of a mixture of the antibiotics and countercurrent distribution in a *n*-butanol–acetic acid–water system (4:1:5) also yielded polyacetylkanamycin B, $[\alpha]_D^{24}$ +107.8 (*c* 0.49, CH_3OH). *Anal.* C, 50.68, 51.05; H, 6.52, 6.61; N, 7.55, 7.68; O-acetyl, 25.4; total acetyl, 46.3; mol. wt., 2010, 2220 (Signer). N-Acetylkanamycin B was obtained by de-O-acetylation with Amberlite IR-410 (OH^-)[2] of the polyacetyl derivative and by acetylation of kanamycin B base in methanol with acetic anhydride. It decomposed gradually at 220° to 250°, $[\alpha]_D^{24}$ +150 (*c* 0.42, H_2O). *Anal.* C, 48.23, 47.97; H, 6.81, 6.78; N, 9.07, 9.14. Kanamycin B yields Schiff bases with aromatic aldehydes as does kanamycin.[1] The N-salicylidene derivative was obtained by treatment of the base in water with an alcoholic solution of salicylaldehyde. *Anal.* C, 58.15; H, 5.60.

Hydrolysis of N-acetylkanamycin B (1 *N* HCl, 40 min. reflux) yielded 2-deoxystreptamine, isolated as the di-N-acetyl derivative and confirmed by infrared comparison with an authentic sample,[1] and kanosamine,[3] isolated as the pentaacetate and confirmed by infrared comparison. Paper chromatograms of acid hydrolyzates of kanamycin B show, in addition to deoxystreptamine and kanosamine, an unidentified ninhydrin-positive reducing spot but no spot for 6-deoxy-6-amino-D-glucose (6-glucosamine).[3] The 6-glucosamine component of kanamycin yields a substance with an ultraviolet spectrum similar to furfural when treated with hot sulfuric acid. Kanamycin B does not give this product, confirming the absence of 6-glucosamine. Both kanamycin B and kanosamine on treatment with 80% sulfuric acid yield a product with the properties of an aminofurfural.

H. SCHMITZ
O. B. FARDIG
F. A. O'HERRON
M. A. ROUSCHE
I. R. HOOPER

RESEARCH DEPARTMENT
BRISTOL LABORATORIES INC.
SYRACUSE, NEW YORK

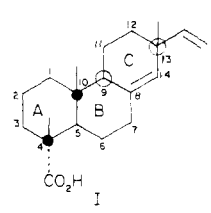
RECEIVED APRIL 1, 1958

(3) M. J. Cron, O. B. Fardig, D. L. Johnson, H. Schmitz, D. F. Whitehead, I. R. Hooper and R. U. Lemieux, THIS JOURNAL, **80**, 2342 (1958).

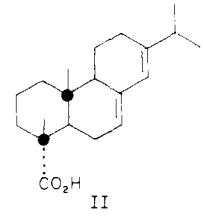
ON THE STEREOCHEMISTRY OF THE PIMARIC ACIDS

Sir:

In view of the stereochemical and possibly biogenetic relationship of pimaric and isopimaric acids (I) with other diterpenes,[1] elucidation of the configuration of especially their 13-substituents is most important.



I



II

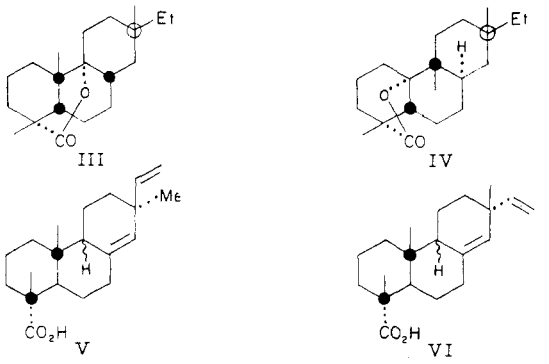
Identical concd. sulfuric acid treatment of pimaric as well as isopimaric acids (I),—−30° for fifteen minutes,—gave the previously reported hydroxylactone,[2] m.p. 180–181°, I.R.($CHCl_3$) 5.75μ, an oily mixture of 5- and 6-membered lactones and abietic acid (II), identified by the characteristic 241 mμ ultraviolet absorption peak and the identity of the infrared spectrum and specific rotation of its di-*n*-amylamine salt with that of an authentic specimen.[3] *These results constitute the first chemical proof of the fact that isopimaric acid is not a racemate*[4] *and represent the first chemical conversion of a pimaradiene to an abietadiene, the final step in the generally accepted biogenesis of abietadienic diterpenes.*[1,5]

Sulfuric acid treatment of dihydropimaric acid at room temperature for ten minutes led to a 1.6:1 mixture of 5- and 6-membered lactones,[6] respectively. Similarly, dihydroisopimaric acid yielded a 1.6:1 mixture of a 5-lactone, m.p. 108–110°,[7] $[\alpha]_D$ −15°, and 6-lactone, m.p. 60–65°, $[\alpha]_D$ −40°. *The production of non-identical sets of lactones from the two dihydro acids under identical conditions of a reaction which perturbs all asymmetric centers except C-4 and 13 proves that the resin acids are at least 13-epimers.*

An infrared spectrophotometric product analysis of an acid-catalyzed equilibration of dihydropimaric acid—concentrated sulfuric acid at room temperature for nineteen hours—indicated the formation of 95 ± 0.6% 6-lactone (III) and 5 ± 0.6% 5-lactone (IV). Equilibration of pure 6-lactone gave the same reaction mixture. However, similar treatment of dihydroisopimaric acid led to a mixture of 96.4 ± 0.8% 6-isolactone (III) and 3.6 ± 0.8% 5-isolactone (IV). *Since the 6-lactones are the more stable products and since the change from the 5- to the 6-lactones involves among other things a conformational inversion at C-13, the system with lower 6-lactone content at equilibrium must have its bulkier*

(1) E. Wenkert, *Chemistry and Industry*, 282 (1955).
(2) E. E. Fleck and S. Palkin, THIS JOURNAL, **62**, 2044 (1940).
(3) G. C. Harris and T. F. Sanderson, *ibid.*, **70**, 334 (1948).
(4) *Cf.* O. Jeger and A. Brossi, *Helv. Chim. Acta*, **33**, 722 (1950).
(5) L. Ruzicka, *Experientia*, **10**, 357 (1953).
(6) (a) T. Hasselström and B. L. Hampton, THIS JOURNAL, **61**, 967 (1939); (b) Le-van-Thoi and J. Ourgaud, *Bull. soc. chim., France*, 1388 (1955).
(7) G. C. Harris and T. F. Sanderson, THIS JOURNAL, **70**, 2081 (1948).

13-substituent in an axial configuration. Thus pimaric acid is V and isopimaric acid VI.[8]



The thus-derived C-13 stereochemistry of the pimaric acids implies that the biosynthesis of ring C takes place in a non-specific manner. Hence, the stereochemistry of tetracarbocyclic diterpenoids, phyllocladene, the aconite alkaloids, etc., cannot be predicted with safety on biogenetic grounds.[9]

(8) The present chemical data corroborate the structural conclusions from surface tension measurements of the pimaric acids [H. H. Brunn, *Acta Acad. Aboensis, Math. et Phys.*, **19**, (3), 7 (1954)]. The authors are most grateful to Mr. L. J. Gough for first drawing their attention to this work.

(9) The authors express their gratitude to Drs. Lawrence and Levan-Thoi and Professor Jeger for gifts of the resin acids and to the Institute for Atomic Research, Ames, Iowa, for the use of a Baird infrared spectrophotometer.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE — ERNEST WENKERT
AMES, IOWA — JAMES W. CHAMBERLIN

RECEIVED APRIL 5, 1958

ACETYLENIC π-COMPLEXES OF CHROMIUM IN ORGANIC SYNTHESIS[1]

Sir:

The concept of the π-complexed intermediate originating from the interaction of sufficiently activated π-electron systems, exemplified previously by aromatic Grignard compounds,[2] with chromium has led to the examination of other π-electron systems and of the prospects of isolating intermediates and final products arising from their reaction with the transition metals. Evidence of the ability of chromium to complex acetylenes and of the fusion of these complexes to aromatic structures has been obtained.[3] The description by Sternberg, Markby and Wender[4] of the use of iron pentacarbonyl in preparing duroquinone constitutes another example of this phenomenon. We now wish to report a specific one-step synthesis of hexamethylbenzene and 1,2,3,4-tetramethylnaphthalene from 2-butyne *via* a π-complex synthesis on chromium as a prototype of a general synthesis of aromatic molecules from acetylenes.

Triphenylchromium tri-tetrahydrofuranate[1] undergoes heterogeneous reaction smoothly with **2-butyne** at 20° within a period of several minutes. Hydrolysis and ether extraction of the mixture are employed to obtain a mixed crystalline product which may be separated by fractional crystallization of the picrates. Under heterogeneous conditions about equal amounts of **hexamethylbenzene,** whose identity was confirmed by mixed m.p. and ultraviolet–infrared spectral comparisons with authentic substance, and **1,2,3,4-tetramethylnaphthalene,** m.p. 107–108.5°, picrate m.p. 183.5–184.5° [*Anal.* Calcd.: C, 91.25; H, 8.75; and C, 58.11; H, 4.63; N, 10.17, respectively. Found: 91.45; H, 8.59; and C, 58.13; H, 4.34; N, 10.55], hithertofore available by a five-step synthesis from prehnitene,[5] are formed.

The condensation of 2-butyne on chromium may also be carried out homogeneously in tetrahydrofuran solution and in this case product control has been found to be possible. For example, if the temperature of the solution is maintained at 0° for 3 days or at room temperature for 3 hours, the sole aromatic product is the naphthalene derivative; and if the solution is maintained at room temperature for 24 hours or heated to reflux for 2 hours, hexamethylbenzene is produced admixed with the naphthalene. However, the formation of the tetramethylnaphthalene in this reaction may be suppressed entirely by the use of triethylchromium in tetrahydrofuran solution with 2-butyne, and in this case the only aromatic product is hexamethylbenzene.

The product, hexamethylbenzene, arising from the reaction between triphenyl- or triethylchromium and 2-butyne clearly requires the intervention of a π-complexed intermediate such as $R_3Cr(CH_3C{\equiv}CCH_3)_3$, this being formed by replacement of the coördinating tetrahydrofuran molecules in $R_3Cr(THF)_3$ by 2-butyne, since this acetylene is unaffected either by chromic trichloride (or its tetrahydrofuranate) or by phenylmagnesium bromide. The participation of the phenyl groups of triphenylchromium in this condensation reaction leading to the naphthalene by interaction of phenyl with two molecules of 2-butyne in the π-complex and consequent *ortho* ring closure opens the way for the synthesis of various condensed aromatic ring systems by an appropriate choice of triarylchromium and acetylene. These reactions will be reported later in detail.

(1) Paper V of "π-Complexes of the Transition Metals"; Paper IV, W. Herwig and H. H. Zeiss, THIS JOURNAL, **79**, 6561 (1957).

(2) H. H. Zeiss and W. Herwig, THIS JOURNAL, **78**, 5959 (1956); *Ann.*, **606**, 209 (1957).

(3) H. H. Zeiss, "Handbook, XVIth International Congress of Pure and Applied Chemistry," July, 1957, Paris, p. 134.

(4) H. W. Sternberg, R. Markby and I. Wender, THIS JOURNAL, **80**, 1009 (1958).

(5) M. C. Kloetzel, R. P. Dayton and H. L. Herzog, *ibid.*, **72**, 273 (1950). Ultraviolet and infrared spectral comparisons confirmed the identity of the two samples.

CENTRAL RESEARCH LABORATORIES
MONSANTO CHEMICAL COMPANY — H. H. ZEISS
DAYTON 7, OHIO — W. HERWIG

RECEIVED MARCH 15, 1958

PHOTOCHEMICAL REACTIONS OF KETONES IN SOLUTION

Sir:

The mechanism of photolysis of ketones has been a subject of current interest,[1-6] and we wish to

(1) W. Davis, Jr., and W. A. Noyes, Jr., THIS JOURNAL, **69**, 2153 (1947).

(2) A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

(3) T. W. Martin and J. N. Pitts, THIS JOURNAL, **77**, 5465 (1955).

(4) P. P. Manning, *ibid.*, **79**, 5151 (1957).

(5) J. R. McNesby and A. S. Gordon, *ibid.*, **80**, 261 (1958).

(6) P. Ausloos, *Can. J. Chem.*, **36**, 400 (1958).