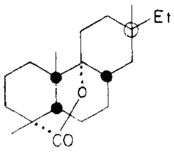
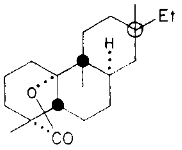
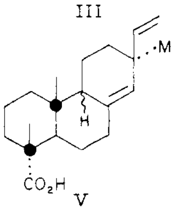
13-substituent in an axial configuration. Thus pimaric acid is V and isopimaric acid VI.[8]



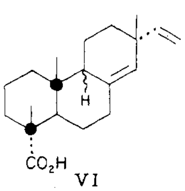
III



IV



V



VI

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]

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[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 Le-van-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.

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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.

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[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.

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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

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[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).