

triphenylphosphine in carbon tetrachloride followed by exhaustive evaporation of the solvent. Fifty ml. of DMF and 1.6 g. (0.018 mole) of neopentyl alcohol were added and the mixture refluxed for 1 hr. The work-up above gave 2.5 g. (92%) of neopentyl chloride, which gave no precipitate with alcoholic silver nitrate; n.m.r.,  $\delta$  (TMS) 1.03 and 3.36 p.p.m. (sharp singlets).

***p*-Chlorobromobenzene.**—Triphenylphosphine dibromide was prepared from 30 g. (0.11 mole) of triphenylphosphine in 100 ml. of acetonitrile. The solvent was evaporated, 10.3 g. (0.08 mole) of *p*-chlorophenol added, and the mixture heated at 200° until no more HBr was evolved (*ca.* 2 hr.). Steam distillation yielded 13.8 g. (90%) of *p*-chlorobromobenzene, which showed a single peak in its gas chromatogram and gave m.p. 64.8–65.5° (uncor.) (lit.<sup>11</sup> m.p. 66°) after crystallization from benzene.

The mechanism of this reaction is under investigation, as well as studies to define its scope, limitations, and stereochemistry.

**Acknowledgment.**—This research was supported in part by Public Health Service Research Grant GM-08956 from the National Institute of General Medical Sciences.

(11) M. L. Sherrill, *J. Am. Chem. Soc.*, **46**, 2756 (1924).

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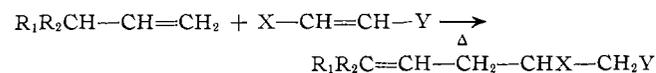
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### Stereochemistry of "No-mechanism" Reactions: Transfer of Asymmetry in the Reaction of Olefins with Dienophiles

Sir:

One of the simplest reactions between organic molecules (though paradoxically ignored in nearly all organic texts) is the thermal addition of olefins to dienophiles. Discovered during the 1930's, the reaction was first investigated thoroughly by Alder and his students<sup>1</sup> and classified as an "indirect substitutive addition"



Like the Diels–Alder addition of dienes to dienophiles, to which it bears a formal resemblance, the reaction has presented the same nearly inscrutable facade to efforts to deduce a detailed mechanism. Early attempts to ascribe to the reaction free-radical<sup>2</sup> or ionic<sup>3</sup> character have been abandoned in favor of a concerted, four-center, cyclic mechanism (Fig. 1), first suggested

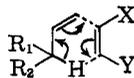


Figure 1.

by Koch<sup>4</sup> and by Arnold and Dowdall.<sup>5</sup> Consequently this addition appears to fall into the category of thermal reorganization processes, aptly described<sup>6</sup> as "no-mechanism" reactions.

(1) K. Alder, F. Pascher, and A. Schmitz, *Ber.*, **76**, 27 (1943); K. Alder and H. von Brachel, *Ann.*, **651**, 141 (1962), and intervening papers.

(2) W. G. Bickford, G. S. Fisher, L. Kyame, and C. E. Swift, *J. Am. Chem. Soc.*, **25**, 251 (1948); E. H. Farmer, *Trans. Faraday Soc.*, **38**, 340 (1942).

(3) (a) C. C. Price, "Mechanisms of Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 50; (b) C. S. Rondstvedt and A. H. Filbey, *J. Org. Chem.*, **19**, 548 (1954).

(4) H. P. Koch, *J. Chem. Soc.*, 1111 (1948).

(5) R. T. Arnold and J. F. Dowdall, *J. Am. Chem. Soc.*, **70**, 2590 (1948).

(6) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

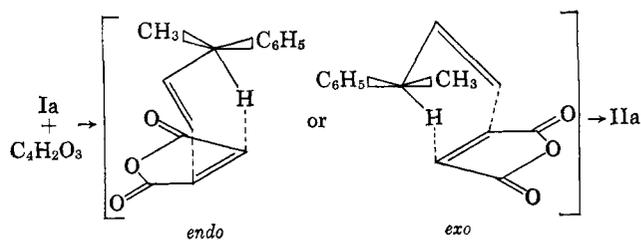
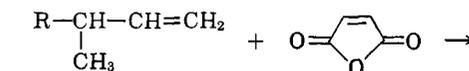


Figure 2.

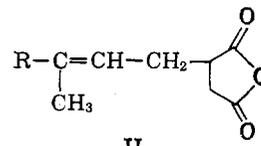
The characteristic and remarkable stereospecificity of the diene addition,<sup>7</sup> and indeed, of other "no-mechanism" reactions such as the Claisen and Cope rearrangements,<sup>6,8</sup> suggested that the transition state for the olefin–dienophile addition might also be a highly oriented one in which the relative bulk of the substituents  $R_1$  and  $R_2$  (in Fig. 1) would play a crucial part in determining the exact geometry.

This expectation has been realized by the finding that use of optically active olefins of type I in the reaction with maleic anhydride leads to optically active products.



Ia,  $R = C_6H_5$

b,  $R = (CH_2)_3CH(CH_3)_2$



II

Heating a solution of (*R*)(–)-3-phenyl-1-butene (Ia),<sup>9</sup>  $[\alpha]_D -6.80^\circ$ , and maleic anhydride in *o*-dichlorobenzene for 12 hr. at 210° led to (3-phenylbuten-2-yl) succinic anhydride (IIa), b.p. 190° (2 mm.),  $[\alpha]_D^{20} -14.5^\circ$ . Optical activity was maintained while the anhydride was hydrolyzed to the acid, m.p. 101–102°,  $[\alpha]_D^{20} 5.9^\circ$ , and converted, by lithium aluminum hydride reduction, to the corresponding diol (bis-*p*-toluenesulfonate, m.p. 99°,  $[\alpha]_D^{20} 2.46^\circ$ ). The structures assigned to these compounds are consistent with their elemental analyses and with their infrared, ultraviolet (maxima at 238–242  $m\mu$ ), and n.m.r. (one olefinic proton) spectra. (*R*)(–)-3,7-Dimethyloctene-1 (Ib),<sup>10</sup>  $[\alpha]_D^{20} -9.30^\circ$ , was heated with maleic anhydride under the same conditions for 20 hr.; distillation of the reaction mixture gave 5,9-dimethyldec-4-ene-1,2-dicarboxylic anhydride (IIb), b.p. 155° (0.2 mm.), which was also optically active,  $[\alpha]_D^{21} -1.90^\circ$ .

Though it is difficult to assess the degree of retention of optical activity during these reactions,<sup>11</sup> several conclusions may be drawn from the results. First, the transfer of optical asymmetry from one of the reactants to a different site in the adduct is fully consistent with a concerted process in which all new bonds are formed essentially simultaneously.

Additional inferences may be drawn by considering the absolute configurations of products IIa and IIb. (–)-IIa displays a plain positive O.R.D. curve, paral-

(7) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

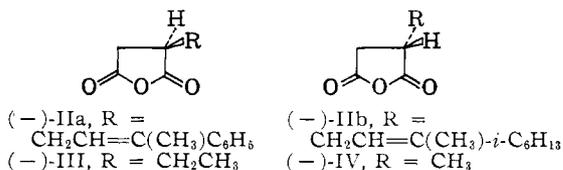
(8) See S. J. Rhoads in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p. 677 ff.

(9) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2137 (1952).

(10) Prepared from (+)-citronellal by a synthesis which will be described in our full paper.

(11) Determination of optical purity of the products is complicated by partial racemization during the reaction. In a model experiment, a 5% solution of (–)-methylsuccinic anhydride in *o*-dichlorobenzene lost 70% of its optical activity on refluxing for 24 hr.

leling the behavior of (*R*)(-)-ethylsuccinic anhydride<sup>12</sup> (III). (-)-IIb, on the other hand, has a plain negative dispersion curve, as does (S)(-)-methylsuccinic anhydride (IV), and so belongs to the enantiomorphous series. The fact that olefins Ia and Ib of opposite configurational series<sup>13</sup> afford products which are also of opposite configuration shows that both olefins react



(12) A. Fredga, "The Svedberg," (Memorial Volume), 1944, p. 261; *Chem. Abstr.*, **39**, 1392 (1945).

(13) For the absolute configuration of Ia, see D. J. Cram and J. Allinger, *J. Am. Chem. Soc.*, **76**, 4516 (1954). The absolute configuration of citronellal, from which Ib is derived, is given by A. J. Birch, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **47**, 192 (1950).

in the same stereochemical sense, regardless of the nature of the group R.

Moreover, using models which correspond approximately to either *endo* or *exo* addition (illustrated in Fig. 2 for the reaction of Ia), it appears that the only orientation of reactants consistent with the stereochemical results is that in which the bulky phenyl (or isohexyl) group is oriented away from the dienophile partner. Orientation thus appears to be governed by simple steric considerations.

Further experiments to verify this mechanism by the use of deuterium-labeled olefins are in progress.

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## BOOK REVIEWS

**Notes on the Thirty-Seventh Annual Priestley Lectures. Some Cosmochemical Problems.** By HAROLD C. UREY, Professor-at-Large of Chemistry, The University of California, San Diego. Mu Chapter Phi Lambda Upsilon and Associated Departments, The Pennsylvania State University, University Park, Pa. 1963. x + 181 pp. 21.5 × 27.5 cm. Price, \$3.25.

The origins of the lunar surface features, of the complexities of meteoritic mineralogy, and of the solar system itself are the problems discussed in this brief survey of the solar system: first a guided tour of the moon, then an outline of the isotopic abundance estimates in the proto-solar system from meteoritic analyses. Two sections cover the formation of the solar system while the last section presents recent ideas on nucleogenesis. Chemistry is prominent in the discussion whether as a tool in the isotopic analysis or more centrally in the examination of the chemistry of iron and the anomalously low density of the earth's core.

These subjects do not allow easy exposition. Unresolved problems abound for every object, while no broad hypothesis organizes the available information coherently. Most readers will be unwilling to make the effort to keep track of meteoritic composition, meteorite by meteorite, phase by phase, isotope by isotope. Yet this is the raw material upon which our understanding must be built.

It is unfortunate that Professor Urey has allowed this to be published as an edited transcription of the recorded lectures. Although it constitutes a reasonable summary of our knowledge in April, 1963, the manner of presentation and careless proof-reading limit this reader's confidence in the text. As such it joins other ephemeral literature (meeting summaries?) as an unreliable, partially redundant, exposition. The author has failed us by his own high standards as expressed in his earlier monograph, "The Planets," (Yale University Press, New Haven, Conn., 1952).

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**Nuclear Chemistry, Technique of Inorganic Chemistry. Volume II.** By NOAH R. JOHNSON, EUGENE EICHLER, and G. DAVIS O'KELLY. John Wiley and Sons, Inc., 605 Third Avenue, New York 16, N. Y. 1963. 202 pp. 16 × 23.5 cm. Price, \$8.00.

"Nuclear Chemistry" sets a new standard of excellence for writing in the field. The level of discussion and organization of material are well suited to inexperienced students and workers desiring to do experiments involving the use of radioactivity. Older workers who have not kept up with the rapid improvement

in techniques and instruments will also find the book very useful. The outstanding attribute of the book is its stress on coherence in the design of experiments—the need to consider the whole experiment when planning each of the steps involved.

The three authors, each with considerable experience in modern nuclear chemistry, have collaborated to produce a concise and uniformly well written text. They give neither microscopic detail nor a catalog of applications, but rather the fundamental principles involved in all applications. For additional details, a carefully selected list of references, most of them to review articles or recent research papers, is given.

The contents include brief discussions of nuclear decay modes, growth-decay relationships, and interactions of radiation with matter, followed by more detailed accounts of the production of radionuclides, chemical separations, and detection devices and techniques. Two general areas merit special attention.

The chapter on "Separation Techniques" is a good example of the emphasis on coherence. An introductory section cautions the reader against pitfalls unique to separations at tracer concentrations. "Strategy of a Separation" demonstrates the need to integrate the separation with the rest of the experiment; that is, the method selected is dependent on the form of the target material, the half-life, and decay properties of the nuclide, and the counting technique to be used. This treatment is a welcome change from the more fragmented "cookbook" approach that characterized much previous writing in the field. The concluding section gives brief coverage of several frequently used separation techniques.

A serious deficiency of most students in nuclear chemistry is the lack of training in electronics. The sections on detection devices and associated electronics will be particularly useful to those in that category. The input- and output-pulse characteristics of a wide variety of detectors and standard "black boxes" are given, along with the pros and cons of each in sufficient detail to allow one to put together the optimum system in most applications. The authors' considerable experience in  $\gamma$ -ray spectroscopy shows up in the exceedingly good description of techniques of that important area.

The only error worthy of mention occurs in the discussion of the mass surface and  $\beta$ -decay energies. Instead of mass excesses, binding energies have been used, but without taking into account the  ${}^1\text{H}^1$ - ${}^0\text{n}^1$  mass difference. This confusion has, unfortunately, been prevalent in the standard textbooks of nuclear chemistry.

In short, "Nuclear Chemistry" is a welcome addition to the field. The reviewer regrets only that the authors have not gone ahead to produce an entire textbook written in the style of this book, as one is sorely needed.

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