

Additions and Corrections

Stable Carbocations. 198. Formation of Allyl Cations via Protonation of Alkynes in Magic Acid Solution. Evidence for 1,2-Hydrogen and Alkyl Shifts in the Intermediate Vinyl Cations [*J. Am. Chem. Soc.*, **98**, 7333 (1976)]. By G. A. OLAH* and H. MAYR, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

Scheme III should read:

R ¹	R ²	
H	H	9
CH ₃	H	11
CH ₃	CH ₃	14
C ₂ H ₅	H	17

Synthesis and Characterization of HO₃(CO)₁₀(CH₃), H₂Os₃(CO)₁₀(CH₂), and H₃Os₃(CO)₉(CH). Interconversion of Cluster-Bound Methyl and Methylene Ligands [*J. Am. Chem. Soc.*, **99**, 5225 (1977)]. By R. BRUCE CALVERT and JOHN R. SHAPLEY,* Department of Chemistry, University of Illinois, Urbana, Illinois 61801.

The ¹³C NMR chemical shifts for HO₃(CO)₁₀(¹³CH₃) and H₃Os₃(CO)₉(¹³CH) should be -59.2 ppm (CD₂Cl₂) and 118.4 ppm ((CD₃)₂CO), respectively. The positions originally reported were due to fold-over peaks. We thank Professor J. R. Norton for bringing the former error to our attention.

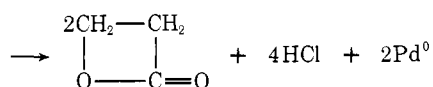
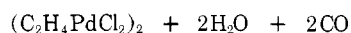
On the Characterization of Transition States by Structure-Reactivity Coefficients [*J. Am. Chem. Soc.*, **99**, 7948 (1977)]. By DAVID A. JENCKS and WILLIAM P. JENCKS,* Graduate Department of Biochemistry, Brandeis University, Waltham, Massachusetts 02154.

Page 7956, column 2, lines 11 and 12 from bottom, replace with:

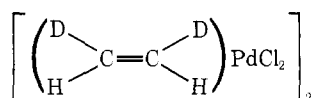
"value of $\rho = 1.03$ for the equilibrium ionization of 1-arylnitroethanes¹⁹ gives a value of $\rho_n = 0.16$, suggesting that there is".

Stereochemistry of the Hydroxypalladation of Ethylene. Evidence for Trans Addition in the Wacker Process [*J. Am. Chem. Soc.*, **100**, 1303 (1978)]. By J. K. STILLE* and R. DIVAKARUNI, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

The incorrect structure for the olefin-palladium(II) chloride complex was inadvertently published; the correct formula is (C₂H₄PdCl₂)₂. Thus, the equation on the formation of β -propiolactone from ethylenepalladium(II) chloride should read:



Accordingly, the structure of the complex derived from *cis*-1,2-dideuterioethylene is:

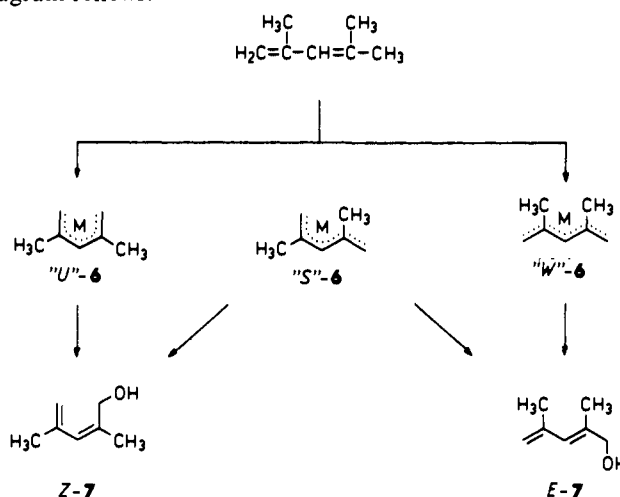


Stereoselectivity and Mechanisms of Acid-Catalyzed Additions of Acetic Acid to (*E*)- and (*Z*)-2-Butene in Acetic Acid [*J. Am. Chem. Soc.*, **100**, 1469 (1978)]. By DANIEL J. PASTO* and JAMES F. GADBERRY, Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.

In Table III the rate constant for addition of acetic acid to (*E*)-2-butene should be $1.37 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ instead of $2.98 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$.

2-Methylpentadienyl- and 2,4-Dimethylpentadienylpotassium: First Examples of U-Shaped, though Open-Chain, Organometallics [*J. Am. Chem. Soc.*, **100**, 3258 (1978)]. By MANFRED SCHLOSSER* and GÜNTER RAUCHSCHWALBE, Institut de Chimie Organique de l'Université, CH-1005 Lausanne, Switzerland.

Page 3259: structures "U"-6 and "W"-6 in the scheme on the top of column one should be interchanged; the correct diagram follows:



A Highly Enantioselective Synthesis of Cyclopropane Derivatives through Chiral Cobalt(II) Complex Catalyzed Carbenoid Reaction. General Scope and Factors Determining the Enantioselectivity [*J. Am. Chem. Soc.*, **100**, 3443 (1978)]. By AKIRA NAKAMURA,* AKIRA KONISHI, YOSHITAKA TATSUNO, and SEI OTSUKA, Department of Polymer Science, Faculty of Science, and the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, 560 Japan.

Parts of the introductory and Results sections were inadvertently omitted from the paper. Since the omission results in inadequate comprehension, the text for two entire sections is reprinted. Structures and tables can be found in the original publication.

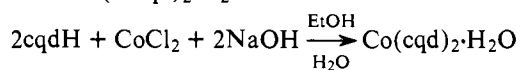
Optically active cyclopropane derivatives have been prepared,³ for example, by the reaction of olefins with stoichiometric amounts of chiral sulfonium ylides (maximum optical yield 30%),⁴ by the Simmons-Smith reactions (CH₂X₂/Zn) employing chiral substrates (optical yield 9.3%),⁵ or by catalytic olefin cyclopropanation with diazoalkanes under the influence of chiral copper complexes (maximum optical yield 8%).^{6,7} In the course of our study on the interaction of diazo

compounds with transition metal compounds,⁸ we have been interested in the asymmetric carbenoid reaction of diazo compounds catalyzed by chiral metal complexes. Among many complexes examined, bis(α -camphorquinonedioximate)-cobalt(II) was found to be an active catalyst for the formation of optically active cyclopropanes with over 80% optical yield. The chemical yield is often in the range 80–95% and only a small amount (1 mol % relative to diazo compound) of catalyst is required. The ready availability of the chiral camphorquinonedioxime ligand from natural sources is also an advantage. Recently, communications⁹ have appeared describing cyclopropanation of 2,5-dimethyl-2,4-hexadiene with various chiral copper chelates with a highly complex ligand (enantioselectivity, 90% max ee).

Since the usefulness of cobalt(II) chelates for catalyzing carbenoid cyclopropanation has been unexplored, we mostly confined our investigations to a cobalt(II) complex of camphorquinonedioxime (cqdH)¹⁰ which is now the best enantioselective catalyst for preparation of *cis*- and *trans*-2-phenylcyclopropanecarboxylic acid. The preparation of the catalyst, details of the reaction, and its general scope and limitations are described in this paper together with a brief discussion of the reaction mechanism. Detailed kinetic studies, catalyst structure, and electronic and steric effects of the reaction will be reported in the subsequent paper.

Results

Various metal(II) complexes (**1** ~ **6**) involving chiral chelate ligands were prepared from optically active amines, β -diketones, or *vic*-dioximes by conventional methods. Structural formulas of these chiral chelates are shown below to indicate the steric environment of the metal. The potential of these complexes as catalysts for the decomposition of ethyl diazoacetate in the presence of styrene was examined. Catalytic cyclopropanation of styrene gave ethyl *cis*- and *trans*-2-phenylcyclopropanecarboxylate in good yield, the optical yield being less than 15%, mostly in a range of 0–6%. Since cobaloxime, Co(dmgl)₂ and its nitrogen base complexes, Co(dmgl)₂Py, were found to be active catalysts, we expected the activity for similar Co(II) compounds of camphorquinone dioximes. Of the four possible geometrical isomers of (1*R*, 4*S*)-bornane-2,3-dione-2,3-dioximes (see below), we have been able to obtain Co(II) complexes of (2*E*, 3*Z*) isomer (α -cqd), (2*E*, 3*E*) isomer (β -cqd), and (2*Z*, 3*E*) isomer (δ -cqd). Remarkably high catalytic activity and high selectivity were realized with Co(α -cqd)₂·H₂O.



(α , β , and δ)

Attempts to obtain a single crystal of the brown air-sensitive compound were unsuccessful. The brown air-sensitive compound, Co(β -cqd)₂·H₂O, was also catalytically active but the enantioselectivity in the carbenoid cyclopropanation was far lower (~20%) than with Co(α - and δ -cqd)₂·H₂O as catalyst. The results of cyclopropanation experiments performed with the Co(α -cqd)₂ catalyst are described below.

Dropwise addition of ethyl diazoacetate to a homogeneous deep brown solution of Co(α -cqd)₂·H₂O in styrene (large excess) at -25° ~ +100° under nitrogen results in vigorous nitrogen evolution. The reaction as monitored by the gas evolution usually takes 1–5 h depending upon the quantities of reagents and the reaction temperature. Distillation of the product gives optically active ethyl 2-phenylcyclopropanecarboxylate which is readily separated into pure *cis* and *trans* isomers by GLC. Each isomer is subsequently hydrolyzed to the corresponding acids. Yields, optical rotations, enantioselectivities and *trans/cis* ratios of the esters and acids obtained under different experimental conditions are summarized in Table I.

The catalyst concentration can be lowered to 1 mol % relative to ethyl diazoacetate without impairing the yield and enantioselectivity. Below 1 mol %, the rate, yield, and optical rotation of the product are low. It is interesting that the selectivity does not improve over 74% for N₂CHCO₂Et even when the reaction temperature is lowered below 20°. This phenomenon will be discussed elsewhere.

Similar reactions of the diazoacetate with various olefins were examined. Olefins with a vinyl or vinylidene group conjugated to an unsaturated center such as C=C, C=O, C≡N, yielded optically active cyclopropane derivatives with Co(α -cqd)₂·H₂O as catalyst. 2-Ethyl-1-butene, *cis*-stilbene, *cis*-2-butene, 2-methyl-2-butene, cyclohexene, 1,3-cyclooctadiene and norbornadiene are not cyclopropanated. Typical results are summarized in Tables II and III. The ¹H NMR spectra of these cyclopropane derivatives are assigned by use of shift reagents (Eu(fod)₃) as shown in Table IV. The assignment was made by considering (1) the distance of the proton in question from the carboxylate group and (2) the ring current effect of the phenyl group. The NMR spectra unambiguously revealed the geometrical structure (*cis* or *trans*) of the cyclopropanes examined.

The result with activated olefins, e.g., methyl acrylate or acrylonitrile, needs comment. The thermal carbenoid reaction of ethyl diazoacetate with these olefins occurs at 20 °C without catalyst to give the corresponding pyrazoline derivatives via 1,3-dipolar cycloaddition. Decomposition of the pyrazoline formed from the acrylate sets in above 60 °C yielding racemic dimethyl cyclopropanedicarboxylate. In the presence of highly active cyclopropanation catalysts Co(α -cqd)₂·H₂O, the reaction in part catalyzed at 22 °C gives a mixture of the cyclopropane and the pyrazoline. Optically active dimethyl *trans*-cyclopropanedicarboxylate was obtained in low yields by distillation of the mixture at 34 °C. Chiral catalysts of lower activity (e.g., Cu[sal(-)pn]) did not give the optically active cyclopropane by direct carbenoid reaction because the uncatalyzed pyrazoline formation occurs first. A similar reaction of acrylonitrile with ethyl diazoacetate at 47–49 °C also proceeds simultaneously via catalyzed and uncatalyzed paths to give mixed *cis/trans*-2-cyanocyclopropanecarboxylate (13% yield) and the corresponding pyrazoline, respectively.

Butadiene or isoprene is cyclopropanated using the same catalyst in an autoclave or in glass pressure tubes to give a *cis/trans* mixture of 2-vinyl- or 2-isopropenyl cyclopropanecarboxylates (Table II) which are not readily separable by GLC. The reaction of *trans*-1-phenyl-1,3-butadiene with ethyl diazoacetate in the presence of Co(α -cqd)₂·H₂O also gave a mixture of *cis*- and *trans*-2-(*trans*-2'-phenylvinyl)cyclopropanecarboxylate in good yields. The absence of the cyclopropanation products at the inner double bond is confirmed by the GLC and ¹H NMR data (see Experimental Section), indicating high regioselectivity. Similar cyclopropanation of isoprene is not very regioselective and a 3:1 mixture of the products involving cyclopropanation at the methylvinyl and vinyl moieties was obtained. Optical yields and absolute configurations of these products from butadiene, isoprene, and *trans*-1-phenyl-1,3-butadiene are unknown, but the [α]_D values (see Table III) are relatively large, suggesting a high degree of enantioselectivity in the catalysis.

The enantioselective cyclopropanation can be extended to other diazoalkanes (cf. Table III). The ester group of the diazoacetate can be varied without any serious effect. An increase in the size of the ester group (methyl, ethyl, isopropyl, neopentyl) gave important information regarding the enantioselection mechanism which is discussed separately in another paper. Diazomethane, diazoacetophenone, and dicyanodiazomethane are catalytically decomposed at 20–40 °C with Co(α -cqd)₂·H₂O. Even highly reactive diazomethane does cyclopropanation selectively with terminal olefins, e.g., styrene,

in the presence of $\text{Co}(\alpha\text{-cqd})_2 \cdot \text{H}_2\text{O}$. The similar reaction in *trans*-1-phenyl-1-propene, however, gave only polymethylene. Bulky diazo compounds such as Ph_2CN_2 or 9-diazo fluorene are not decomposed even above 60 °C. The reaction of dicyanodiazomethane with styrene proceeded at 35 °C to give 2-phenyl-1,1-dicyanocyclopropane in 20% yield. The enantioselectivity was only 4.6% and side reactions predominated. Diazoacetophenone and styrene also give a mixture of *cis*- and *trans*-2-phenyl-1-benzoylcyclopropane (cf. Table III). The *trans* isomer was obtained in an optical yield of 20%, which is considerably lower than the value obtained with diazoacetates. The optical rotation and configuration of the optically pure *cis* isomer are unknown.

Although most of the reactions have been performed in neat olefin, it is possible to dilute the reaction mixture with usual organic solvents, such as ethyl acetate, to an extent of ~3 M for the olefin concentration. Further dilution deactivates the catalyst and retards very much the reaction rate. The results in Table V show that the enantioselectivity does not decrease

appreciably in most cases. Use of more strongly coordinating solvents such as pyridine or picolines decreases the activity and selectivity. Effects of these additives will be fully described separately.

Solvent Effects on Protomeric Equilibria: Quantitative Correlation with an Electrostatic Hydrogen-Bonding Model [*J. Am. Chem. Soc.*, **100**, 3961 (1978)]. By PETER BEAK* and JOHNNY B. COVINGTON, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801.

Page 3961, lines 20 to 23 should read: 6-chloro-2-thiopyridine (**6a**)-6-chloro-2-thiopyridone (**6b**), 2-thiopyridine (**5a**)-2-thiopyridone (**5b**), and 4-thiopyridine (**7b**)-4-thiopyridone (**7d**).

Table I: the heading of last column should be **7c** and **7d**; the first column, line 12, *n*-butyl; line 14, *n*-propyl; line 16, methyl.

Page 3962, column 2, line 3: read **4c-4d** for **4a-4b**.

Book Reviews*

Pesticides. An Auto-Tutorial Approach. By GEORGE W. WARE (University of Arizona). W. H. Freeman and Co., San Francisco, Calif. 1975. xv + 191 pp. \$5.95.

This paperbound book is based on the author's "programmed learning" lectures and is designed to give the layman "an appreciation for the fine state of this segment of chemical art and science." It might be a good book for chemists to recommend when acquaintances without professional chemical background ask about modern agricultural chemicals. It not only treats the many different types of pesticides from the standpoint of structure and function, but places the subject in perspective, with sections on legal aspects, toxicity, and safe handling.

Resinography. By T. G. ROCHOW and E. G. ROCHOW. Plenum Press, New York, N.Y. 1976. xiv + 187 pp. \$25.00.

This book is subtitled "An Introduction to the Definition, Identification, and Recognition of Resins, Polymers, Plastics and Fibers." The authors point out that resinography is a comparison discipline to metallography and petrography and often uses the same instruments and investigative techniques. A course which they gave at the School of Textiles, North Carolina State University at Raleigh, provided the basis for this book, which may be the first on the subject. Their approach is more that of materials science than chemistry, but the subject is obviously one of importance to chemists concerned with plastics and their applications.

Compendium of Organic Synthetic Methods. Volume III. By L. S. HEGEDUS and L. G. WADE. John Wiley/Interscience, New York, N.Y. 1977. xv + 495 pp. \$17.00.

This immensely useful work reaches its third volume with new authors, but is otherwise essentially unchanged. It presents in equation form, with clearly written structure, transformations of functional groups, and preparations of difunctional compounds, taken from the literature of 1974, 1975, and 1976. Access to specific information is actually fairly easy by scanning, but the organization of chapters by functional group prepared, and within each chapter, by kind of starting material, makes quick access possible. As in previous volumes, only yield and reference are given beside the equation itself.

Handbook of Nonprescription Drugs. Fifth Edition. Edited by R. P. PENNA and C. KLEINFELD. American Pharmaceutical Association, Washington, D.C. 1977. xiii + 387 pp. \$12.50.

This book is intended to be a reference for practical information for use by pharmacists and others in related health care fields. It is composed of 32 contributed chapters, on such subjects as Laxative Products, Dental Products, etc., in which function and recommended use are given primary attention.

The Nature of Seawater. Edited by EDWARD D. GOLDBERG. Dahlem Konferenzen, Delbrückstr. 4C, D-1000 Berlin 33, W. Germany. 1975. 719 pp. \$?

This soft-bound volume is the proceedings of an international conference held in 1975. It consists of papers and group reports, largely of a review nature. They are well illustrated and documented, and include many tables. The scope of the conference was wide enough to include such important topics as biodegradation of petroleum hydrocarbons, and biogenesis of halogenated sesquiterpenes. An extensive index increases its reference value.

Chemical Process Industries. Fourth Edition. By R. N. SHREVE and J. A. BRINK, JR. McGraw-Hill Book Co., New York, N.Y. 1977. 814 pp. \$23.75.

This is a book for chemical engineers and for those chemists and others who want to find out something about the major chemical manufacturing processes. The material is presented in 40 concise chapters, on such subjects as "electrothermal industries", pharmaceutical industries", etc. The book contains enormous amounts of data in tables and has many diagrams and illustrations, including one of an early type of uranium bomb. Although this edition is said to have been extensively rewritten, the chemistry presented does not show it. Along with quite correct structural formulas, there are whole sections that have been unchanged from the 1930's, showing benzene rings as cyclohexane rings. Proofreading of the chemistry appears to have been nonexistent, and such abominations as " $\text{CH}_2=\text{CCl}=\text{CH}=\text{CH}_2$ " for chloroprene are common. It is a pity that an otherwise good work is so marred.

Aromatic and Heteroaromatic Chemistry. Volume 5. Senior Reporters: C. W. BIRD and G. W. H. CHEESEMAN. The Chemical Society, London. 1977. xv + 566 pp. \$70.00.

This volume reviews the literature published between July 1975 and June 1976. The well-known chemists in the list of 13 reporters have demonstrated by the substantial efforts they have contributed how important they consider this activity of The Chemical Society to be.

The chapter topics are imaginative and draw one's interest; in addition to the obvious topics, there are chapters on ring transformations,

* Unsigned book reviews are by the Book Review Editor.