solvent B. A 1-in. wide strip of the chromatogram was used for the paper chromatogram scanner for locating the radioactive bands. For identification of end groups, the material in the original peak or the purified band was kept in 1 N potassium hydroxide for 24 hr. at room temp. and then the total passed through a short column of pyridinium Dowex-50 ion exchange resin column and the column washed with 10% aqueous pyridine. The total effluent was evaporated and the products separated by paper

electrophoresis at pH 5 in freshly made 0.1 M ammonium acetate buffer. The Anil-pGp or Anil-pAp band traveled ahead of the major nucleotide bands. The bands were eluted and the material freed from salt and further examined by paper chromatography in solvent B. Standard markers of nucleotides and the anilidates were applied alongside. In addition to identification by radioactive scanning, the spots were eluted and characterized by ultraviolet absorption spectra and specific radioactivity.

COMMUNICATIONS TO THE EDITOR

The Atom Connectivity Matrix (ACM) and its Characteristic Polynomial (ACMCP): A New Computer-Oriented Chemical Nomenclature

Sir:

The Atom Connectivity Matrix, or ACM, here described, is a new unambiguous universal symbolism which, with only two simple rules, allows ready transformation, even by non-professionals, of the usual two dimensional pictorial molecular representation (or even more sophisticated models) into a unique mathematical expression readily useful for hand or computer manipulation.
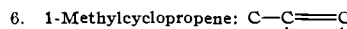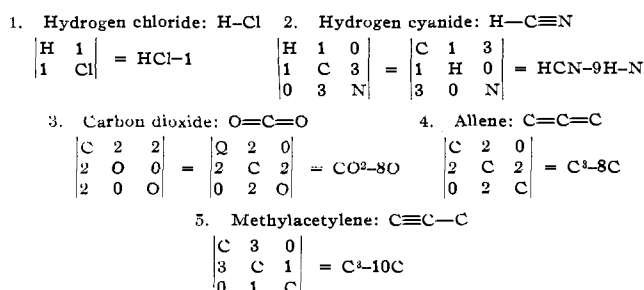
Rule I.—Sketch the molecule with all the atoms (or radicals or nuclides) and interatomic connectivities (bonds, bond orders, force constants, ionic character, dipole moments, or vectorial components) desired to be incorporated into the ACM. Atoms and connectivities should be indicated in the pictorial representation. Anything from skeletal stick formulas to more complicated structures may be written.

Rule II.—Construct a matrix array, the ACM, wherein the a_{ii} elements (those on the matrix diagonal from upper left to lower right) represent the constituent atoms (defined above) and the off-diagonal a_{ij} elements represent the connectivity between the ith and jth atoms. The order of writing the diagonal elements is unimportant.

The characteristic polynomial, ACMCP, obtained by evaluating the ACM as a determinant, is invariant with respect to direction of viewing the molecule and order of numbering the atoms, and has a unique one-to-one correspondence with its pictorial progenitor.

The ACM (and its ACMCP) is versatile and universal in that any order of approximation may be selected, depending upon the molecular details to be represented. A few arbitrarily designated types of approximations and representative examples are:

A. Zero-Order Approximation.—Only the basic linked backbone atoms are listed (hydrogen may be omitted in organic molecules, or fluorine in fluorocarbons, or repeating groups in ionic structures) and the connectivities between pairs of atoms are assigned integral bond order values of 0, 1, 2 and 3 for no, single, double and triple bonds, respectively.

1. Hydrogen chloride: H–Cl

$$\begin{vmatrix} H & 1 \\ 1 & Cl \end{vmatrix} = HCl-1$$

2. Hydrogen cyanide: H—C≡N

$$\begin{vmatrix} H & 1 & 0 \\ 1 & C & 3 \\ 0 & 3 & N \end{vmatrix} = \begin{vmatrix} C & 1 & 3 \\ 1 & H & 0 \\ 3 & 0 & N \end{vmatrix} = HCN-9H-N$$

3. Carbon dioxide: O=C=O

$$\begin{vmatrix} C & 2 & 2 \\ 2 & O & 0 \\ 2 & 0 & 0 \end{vmatrix} = \begin{vmatrix} O & 2 & 0 \\ 2 & C & 2 \\ 0 & 2 & 0 \end{vmatrix} = CO^2-8O$$

4. Allene: C=C=C

$$\begin{vmatrix} C & 2 & 0 \\ 2 & C & 2 \\ 0 & 2 & C \end{vmatrix} = C^3-8C$$

5. Methylacetylene: C≡C—C

$$\begin{vmatrix} C & 3 & 0 \\ 3 & C & 1 \\ 0 & 1 & C \end{vmatrix} = C^3-10C$$

6. 1-Methylcyclopropene: C—C=C (ring with C)

$$\begin{vmatrix} C & 1 & 0 & 0 \\ 1 & C & 2 & 1 \\ 0 & 2 & C & 1 \\ 0 & 1 & 1 & C \end{vmatrix} = \begin{vmatrix} C & 2 & 1 & 1 \\ 2 & C & 1 & 0 \\ 1 & 1 & C & 0 \\ 1 & 0 & 0 & C \end{vmatrix} = C^4-7C^2 + 4C + 1$$
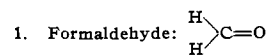
7. 2-Methylcyclopropene: (ACMCP identical with 6 above)

8. 3-Methylcyclopropene: C=C (ring) C–C

$$\begin{vmatrix} C & 1 & 0 & 0 \\ 1 & C & 1 & 1 \\ 0 & 1 & C & 2 \\ 0 & 1 & 2 & C \end{vmatrix} = C^4-7C^2 + 4C + 4$$

9. Alkyl bromide: R–Br

$$\begin{vmatrix} R & 1 \\ 1 & Br \end{vmatrix} = RBr-1$$

B. First-Order Approximation.—This is the same as the zero-order A above, but includes all atoms.

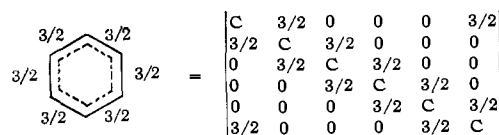1. Formaldehyde: $\begin{smallmatrix} H \\ H \end{smallmatrix}$C=O

$$\begin{vmatrix} H & 0 & 1 & 0 \\ 0 & H & 1 & 0 \\ 1 & 1 & C & 2 \\ 0 & 0 & 2 & 0 \end{vmatrix} = H^2CO-4H^2-2HO$$

C. Higher-order approximations may include fractional bond orders (which may be desirable for delocalized aromatic and sandwich-type molecules), directed or vectorial connectivities, etc. In most cases, these would be less commonly used than the simpler types above.

As examples of other atoms or connectivity types used to develop appropriate ACM's, the following are shown:

Delocalized benzene, where the C–C bond order is 3/2.

$$= \begin{vmatrix} C & 3/2 & 0 & 0 & 0 & 3/2 \\ 3/2 & C & 3/2 & 0 & 0 & 0 \\ 0 & 3/2 & C & 3/2 & 0 & 0 \\ 0 & 0 & 3/2 & C & 3/2 & 0 \\ 0 & 0 & 0 & 3/2 & C & 3/2 \\ 3/2 & 0 & 0 & 0 & 3/2 & C \end{vmatrix}$$

Note: The above ACM differs from that for the Kekulé or that for the Dewar forms since the ACM is always the exact analog of the pictograph selected.

Localized free radicals, such as ethyl radical, require an added symbol, ϵ, for the electron

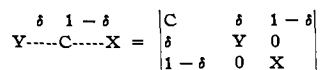$$\cdot C–C = \begin{vmatrix} C & 1 & 0 \\ 1 & C & 1 \\ 0 & 1 & \epsilon \end{vmatrix}$$
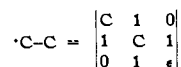
Linked rings, A and B, where no direct bonding occurs but integrity of each ring is required for existence of the molecule are exemplified by

$$(A)(B) = \begin{vmatrix} (ACM)_A & 0 \\ 0 & (ACM)_B \end{vmatrix}$$
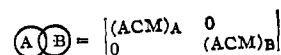
where $(ACM)_A$ and $(ACM)_B$ are the ACM's for A and B respectively. Note: This principle of zero-order delocalized bonds is appropriate for clathrates, inclu-

sion compounds, molecular complexes, and approximations to n-mer polymers.

Transition states require a variable bond order, δ, as a reaction parameter which varies from 0 to 1 during the reaction. The skeletal picture of a transition state for a displacement reaction can be described as

$$Y\text{-----}C\text{-----}X = \begin{vmatrix} C & \delta & 1-\delta \\ \delta & Y & 0 \\ 1-\delta & 0 & X \end{vmatrix}$$

$$\overset{\delta}{}\overset{1-\delta}{}$$

Of course, larger molecules generate larger ACM's. However, assembly of the array is not any more complicated, and, since the sum of atomic connectivity terms generally does not exceed about 4 or 5 for most atoms, a large number of off-diagonal zero elements is found. These latter simplify computation.

The ACMCP's may be evaluated by hand or, when large, more conveniently by computers. It is merely necessary to maintain the identity of the different types, only, of the atoms. This can be done by direct numerical or letter address or by other artifices, such as the assignment of large primes in ordered fashion to the atoms or nuclides of the periodic system.

It will be noted that the first term of the characteristic polynomial ACMCP is identical with the usual simple molecular formula except that the subscripts have now become superscripts (analogous to the French style). Hence, cataloging and searching is compatible with current formula indices.

For computer input and information retrieval from memory, one can either use the ACM (transformed internally into the ACMCP) or the ACMCP (or fractional part thereof). For memory storage, the ACMCP has many advantages over the ACM, particularly in its invariance and its ready fractionation for homolog, derivative, and classification purposes. For encoding, the ACM is preferable.

Further details of molecular coding and search, ACMCP fractionation and interpretation, reaction coding, orders of approximation and application to other molecular types (including ions with directed bonds, homologs, ions, radicals, polymers, clathrates, geometrical and stereoisomers, etc.) will appear in more detailed form elsewhere.

CHEMISTRY RESEARCH LABORATORY, ARL   LEONARD SPIALTER
WRIGHT-PATTERSON AF BASE, OHIO
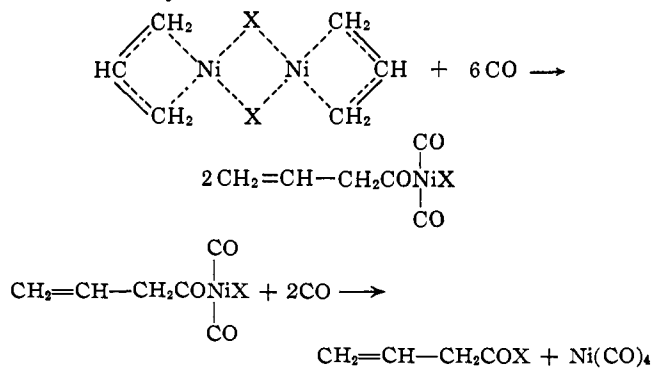   RECEIVED APRIL 13, 1963

The Mechanism of the Allyl Halide Carboxylation Reaction Catalyzed by Nickel Carbonyl

Sir:

The carboxylation of π-allylnickel bromide dimer in methanol solution has been reported recently by Fischer[1] and Chiusoli.[2] The product of the reaction, methyl 3-butenoate,[2] apparently was first identified incorrectly as methyl methacrylate.[1] We find the reaction proceeds under very much milder conditions than were used by the above workers. Carrying out the reaction under the milder conditions in an inert solvent has given considerably more information about the mechanism of the reaction.
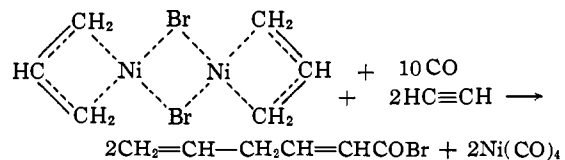
π-Allylnickel iodide dimer as an 0.085 M solution in ether at 0° absorbed nearly 10 moles of carbon monoxide per mole of dimer in less than 1.5 hr. The infrared spectrum of the reaction mixture has a very strong carbonyl band at 4.90 μ, undoubtedly produced by nickel carbonyl, and a weak band at 5.65 μ from 3-butenoyl iodide, identified by converting it to the methyl ester with methanol and analyzing by vapor

(1) E. O. Fischer and G. Burger, *Z. Naturforsch.*, **17b**, 484 (1962).
(2) G. P. Chiusoli and S. Merzoni, *ibid.*, **17b**, 850 (1962).

phase chromatography. No methyl crotonate or methacrylate was found in the reaction mixture. Similarly, π-allylnickel bromide absorbed carbon monoxide, but more slowly. There was a definite decrease in the rate of gas absorption after about two-thirds of the carbon monoxide had been absorbed. At this point, the infrared spectrum had a strong, new, coordinated carbonyl band at 4.78 μ and another new, weak carbonyl band at 5.72 μ. These are the absorptions expected for a butenoylnickel dicarbonyl bromide intermediate. After completion of the carbon monoxide absorption, only the nickel carbonyl band at 4.90 μ and the acyl bromide band at 5.54 μ were visible. π-Allylnickel chloride dimer, which can be prepared by heating allyl chloride and nickel carbonyl in benzene solution at 70° for an hour and evaporating the solution below room temperature, is a very unstable compound but it can be kept in ether solution at 0° for a considerable length of time. This material reacts very rapidly with carbon monoxide to form the butenoylnickel dicarbonyl chloride (infrared bands at 4.75 and 5.75 μ), and much more slowly to form the butenoyl chloride and nickel carbonyl.

$$\underset{HC}{\overset{CH_2}{\diagup}}\underset{CH_2}{\overset{X}{\diagup}}\underset{Ni}{\diagdown}\underset{X}{\diagup}\underset{Ni}{\diagdown}\underset{CH_2}{\diagup}CH + 6\,CO \longrightarrow$$

$$2\,CH_2{=}CH{-}CH_2\overset{CO}{\underset{CO}{\overset{|}{\underset{|}{C}}}}NiX$$

$$CH_2{=}CH{-}CH_2\overset{CO}{\underset{CO}{\overset{|}{\underset{|}{C}}}}NiX + 2CO \longrightarrow$$

$$CH_2{=}CH{-}CH_2COX + Ni(CO)_4$$

An attempt to isolate a stable triphenylphosphine derivative of the acylnickel dicarbonyl chloride by adding excess triphenylphosphine to the acylnickel solution led to the formation of a bright red, insoluble compound, but the complex decomposed on attempted isolation into the known π-allylnickel triphenylphosphine chloride.[3]

A mixture of acetylene and carbon monoxide reacts with π-allylnickel bromide dimer at 0° in ether solution to give nickel carbonyl and a carbonyl compound with absorption at 5.61 μ. Since about 12 moles of gas was absorbed, the carbonyl compound is probably 2,5-hexadienoyl bromide. There was no evidence for an

$$\underset{HC}{\overset{CH_2}{\diagup}}\underset{CH_2}{\overset{Br}{\diagup}}\underset{Ni}{\diagdown}\underset{Br}{\diagup}\underset{Ni}{\diagdown}\underset{CH_2}{\diagup}CH + \begin{array}{l}10\,CO \\ + \\ 2HC{\equiv}CH\end{array} \longrightarrow$$

$$2CH_2{=}CH{-}CH_2CH{=}CHCOBr + 2Ni(CO)_4$$

intermediate in this example, although an acylnickel dicarbonyl bromide must surely be involved.

These reactions are clearly the ones involved in Chiusoli's catalytic carboxylation of allylic halides and in the addition of acetylene and carbon monoxide to allylic compounds.[4] It is also very likely that similar reactions are involved in both the nickel-catalyzed olefin–carboxylation reaction[5] and in the acrylate synthesis.[6] These carboxylation reactions proceed best in the presence of traces of acids, particularly hydrogen

(3) R. F. Heck, J. C. W. Chien and D. S. Breslow, *Chem. Ind.* (London). 467 (1960).
(4) G. P. Chiusoli, *Angew. Chem.*, **72**, 74 (1960); *Chim. Ind.* (Milan), **43**, 259, 638 (1961).
(5) W. Reppe and H. Kröper, *Ann.*, **582**, 38 (1953).
(6) W. Reppe, *ibid.*, **582**, 1 (1953).