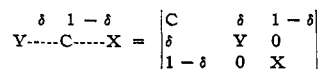


sion compounds, molecular complexes, and approximations to n -mer polymers.

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



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

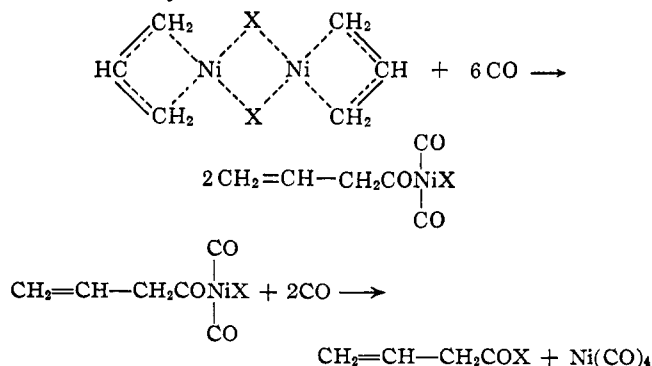
The Mechanism of the Allyl Halide Carboxylation Reaction Catalyzed by Nickel Carbonyl

Sir:

The carboxylation of π -allylnickel bromide dimer in methanol solution has been reported recently by Fischer¹ and Chiusoli.² The product of the reaction, methyl 3-butenolate,³ 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.

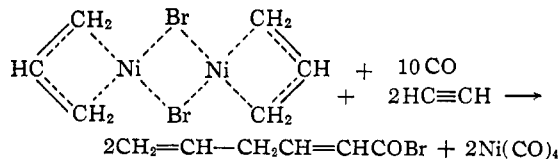
π -Allylnickel iodide dimer as an 0.085 M solution in ether at 0° absorbed nearly 10 moles of carbon monoxide per mole of dimer in less than 1.5 hr. The infrared spectrum of the reaction mixture has a very strong carbonyl band at 4.90 μ , undoubtedly produced by nickel carbonyl, and a weak band at 5.65 μ from 3-butenoyl iodide, identified by converting it to the methyl ester with methanol and analyzing by vapor

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.



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



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 reaction⁵ 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).

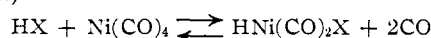
(5) W. Reppe and H. Kröper, *Ann.*, **582**, 38 (1953).

(6) W. Reppe, *ibid.*, **582**, 1 (1953).

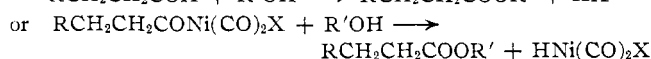
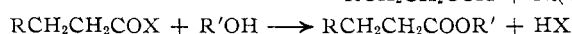
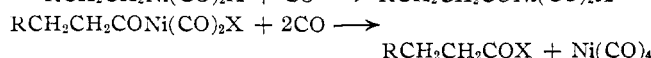
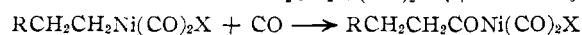
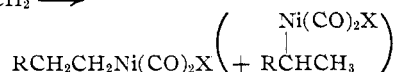
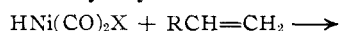
(1) E. O. Fischer and G. Burger, *Z. Naturforsch.*, **17b**, 484 (1962).

(2) G. P. Chiusoli and S. Merzoni, *ibid.*, **17b**, 850 (1962).

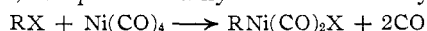
halides.^{5,6} It is likely that the halogen acid is required to produce a halonickel dicarbonyl hydride which is the true catalyst. (Other acids could produce analogous hydrides.)



The hydride could then add to the olefin (or acetylene) to give an alkylnickel dicarbonyl halide; this could absorb carbon monoxide and form the acylnickel dicarbonyl halide. The final step could either be elimination of acyl halide with the re-formation of nickel carbonyl, or possibly direct alcoholysis of the acyl compound to ester (or acid) and the halonickel dicarbonyl hydride.



An alternative initial step would be the formation, from the halogen acid and olefin, of alkyl halide which then reacts directly with nickel carbonyl, as allylic halides do,⁷ to produce alkylnickel dicarbonyl halides.



Both of these initial steps have analogies in other group VIII metal reactions. Hydrogen chloride adds to bis-(triphenylphosphine)-carbonyl chloroiridium to give bis-(triphenylphosphine)-carbonyl dichloroiridium hydride⁸ and methyl iodide adds to bis-(triethylphosphine)-iodo-(methyl)-platinum to form bis-(triethylphosphine)-diiodo-(dimethyl)-platinum.⁹ In either case, the subsequent steps are similar to those proposed to explain the hydroformylation reaction,¹⁰ with hydrolysis or alcoholysis replacing hydrogen reduction.

Attempts to detect intermediates in the olefin or acetylene carboxylation reactions have not been successful because the nickel carbonyl does not react with hydrogen halides or alkyl halides at low temperatures. At higher temperatures, the intermediates react further as they are formed and cannot be observed.

(7) E. O. Fischer and G. Burger, *Z. Naturforsch.*, **16b**, 77 (1961); *Chem. Ber.*, **94**, 2409 (1961).

(8) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 679 (1962).

(9) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).

(10) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

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RECEIVED APRIL 5, 1963

Variation of Vinyl Proton Coupling Constants with Ring Size in *cis*-Cyclic Olefins

Sir:

Calculations based on the Karplus equation relating dihedral angle and coupling constant suggest that all *cis*-disubstituted olefins (dihedral angle 0°) should show vinyl proton coupling constants of 6.1 c.p.s. while *trans*-disubstituted olefins (dihedral angle 180°) should show vinyl proton coupling constants of 11.9 c.p.s.¹ The ratio of $J_{\text{cis}}/J_{\text{trans}}$ is consistent with the experimental for ethylene² but the predicted values³ are substantially

(1) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).























(2) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc. (London)*, **A269**, 385 (1962).

(3) The agreement is improved by consideration of σ - π interaction which adds 1.5 c.p.s. to the predicted values: M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

TABLE I
SUMMARY OF VARIATION OF VINYL PROTON COUPLING CONSTANT WITH RING SIZE IN *cis*-CYCLIC OLEFINS

Ring size	Range of coupling constants	No. of examples
8	11.8-12.8	3
7	9.7-12.5	6
6	9.9-10.5	15
5	5.4-7.0	16
4	2.5-3.7	8

TABLE II
VINYL PROTON COUPLING CONSTANTS OF *cis*-CYCLIC OLEFINS

Structure	Ring size	$J_{\text{vinyl protons}}$ (c.p.s.) ^a
	4	2.5
	4	2.5
	4	2.8
	5	6.0
	4	2.7
	5	... ^b
	4	2.8
	6	... ^b
	4	2.9
	5	... ^b
	4	3.7
	4	2.9
	5	5.6
	4	... ^c
	5	6.0
	5	6.3
	5	6.0
	5	7.0 ^d
	5	6.0 ^d
	5	6.0
	5	7.0
	5	6.3