pounds and other rigid systems, where the dihedral angle is known, will furnish further information on the problem.

It was pointed out previously[6] that, within the same compound, $J_{\mathrm{C^{13}-C-C-H}}$ is occasionally larger in magnitude than $J_{\mathrm{C^{13}-C-H}}$. Table I shows that such anomalous spin–spin couplings seem to be the rule rather than the exception in compounds where the C^{13} is sp^3-hybridized.[13]

We wish to point out that changes in the hybridization of the carbon atoms through which the coupling is transmitted result to unusually large coupling (last two cases in Table I).

Experimental

Preparation of C^{13}-Labeled Compounds.—All labeled compounds were synthesized according to well established preparative methods. Three compounds, diethyl ketone-*carbonyl*-C^{13} (Isotopes Specialties Co., Calif.), methyl propionate-*carbonyl*-C^{13} (Isotopes Specialties Co., Calif.) and methyl iodide-C^{13} (Isomet Corporation, N. J.) served as starting materials.

a. **Propionic acid-1-C^{13}** was prepared by saponification of methyl propionate-*carbonyl*-C^{13}, acidification, extraction with ether, evaporation of ether and collection through a Beckman Megachrom.

b. **3-Deuterio-3-pentanol-3-C^{13}** was prepared by reduction of diethyl ketone-*carbonyl*-C^{13} with lithium aluminum deuteride. Purification of product was achieved by collection through Megachrom.

c. **1,1-Dideuterio-1-propanol-1-C^{13}** was prepared by reduction of methyl propionate-*carbonyl*-C^{13} with lithium aluminum deuteride. Product purification was achieved by use of Megachrom.

d. **3-Ethyl-3-pentanol-3-C^{13}** was prepared from ethyl magnesium bromide and diethyl ketone-*carbonyl*-C^{13}.

e. **Ethyl acetate-carbonyl-C^{13}** was given to us by Dr. R. L. Schwendeman.

f. **C^{13}-Labeled *t*-Amyl Alcohols and *t*-Amyl Chlorides.**—The preparation of these compounds will be reported elsewhere.

g. **2,4-Dinitrophenylhydrazone and semicarbazone** of diethyl ketone-*carbonyl*-C^{13} were prepared by conventional methods and recrystallized from absolute ethanol.

Measurements.—All spectra were taken with a model V4300-2 Varian Associates high resolution n.m.r. spectrometer at 60 Mc. Solutions of about 20% of the labeled compounds in carbon tetrachloride were used with the following exceptions: Diethyl ketone, methyl propionate and the *t*-amyl chlorides were examined as neat liquids. The spectra of 2,4-dinitrophenylhydrazone and the semicarbazone of diethyl ketone were taken in nitrobenzene and chloroform. In all cases thin-walled Wilmad Glass Co. tubes were used. Spin–spin coupling constants were measured using the standard side band technique,[14] a frequency counter being employed.

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[13] We have been informed (P. T. Narasimhan, private communication) that $J_{\mathrm{C_{13}—C-H}}$ is negative while $J_{\mathrm{C_{13}-C-C-H}}$ is positive.

[14] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS, LAWRENCE, KAN.]

Addition of Weak Acids to Vinylmetallocenes

BY GLEN R. BUELL, WILLIAM E. MCEWEN AND JACOB KLEINBERG

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The addition of absolute acetic acid and of hydrogen azide to vinylferrocene has been shown to proceed in accordance with Markownikoff's rule. These addition reactions, which occur even at room temperature, demonstrate an unusual reactivity of the vinyl group. Vinylruthenocene and vinylosmocene have been prepared and these compounds also add absolute acetic acid readily. The rates of addition of acetic acid to the three vinylmetallocenes have been measured and fall in the relative order 4.62:1.19:1.00 for vinylosmocene:vinylruthenocene:vinylferrocene. These results indicate that the α-metallocenyl transition carbonium ions possess unusual stability relative to ordinary carbonium ions derivable from 1-alkenes in addition reactions.

In a preliminary communication[1] from this Laboratory it was reported that hydrogen azide and also acetic acid readily add across the double bond of vinylferrocene. This extraordinary reactivity of the vinyl group was so striking that we decided to extend the investigation to vinylruthenocene and vinylosmocene and to determine the rates of addition of absolute acetic acid to the three vinylmetallocenes.

The uncatalyzed addition of weak acids to olefins does not generally occur readily, and there is little information on the subject in the literature. Fort and Girard[2] have shown that anhydrous formic acid adds to alkenes, such as 1-octene, at 80°, according to Markownikoff's rule. These investigators have provided evidence that the mechanism of addition is analogous to that of the addition of strong acids to olefins.[3] Specifically, a π-complex between the proton of the acid and the olefin is first formed, and this rearranges to a carbonium ion, which then adds the formate ion. Chablay[4] has found that *t*-amyl acetate may be obtained in 4% yield by treatment of trimethylethylene with absolute acetic acid at 125° for 200 days.

In our preliminary paper[1] we reported that vinylferrocene, prepared by the method of Arimoto and Haven,[5] undergoes reaction with a solution of hydrogen azide and absolute acetic acid in benzene to give a mixture of α-ferrocenylethyl azide, a relatively small quantity of a second, unidentified azide, α-ferrocenylethyl acetate and acetylferrocene. α-Ferrocenylethyl azide was characterized by its conversion to the known α-ferrocenylethylamine[6] under conditions of catalytic hydrogenation, by preparation of the same azide from α-ferrocenylethyl alcohol by reaction with hydrogen azide under the same conditions as used in the addition of the acid to vinylferrocene, and by the presence of an

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[1] G. R. Buell, W. E. McEwen and J. Kleinberg, *Tetrahedron Letters*, No. **5**, 16 (1959).

[2] A. W. Fort and C. A. Girard, *Petroleum Research Fund Report*, 42 (1958); 27 (1959).

[3] R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 5372 (1952).

[4] A. Chablay, *Compt. rend.*, **250**, 2722 (1960).

[5] F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **77**, 6295 (1955).

[6] P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson and G. M. Whitman, *ibid.*, **79**, 3416 (1957).

infrared absorption peak in carbon disulfide solution at 4.80 μ, characteristic of the azido group.

There is good reason to believe that the acetylferrocene, which was isolated by chromatography of the reaction products on alumina, arose as a result of the decomposition of α-ferrocenylethyl azide to the corresponding imine, with subsequent hydrolysis of the latter. Whenever the *pure* azide was permitted to stand for some time and then rechromatographed, acetylferrocene was obtained in addition to the azide. As a matter of fact, α-ferrocenylethyl acetate was not isolated as such in this experiment, but rather as the carbinol. It was found in independent experiments that α-ferrocenylethyl acetate underwent hydrolysis on an alumina column to α-ferrocenylethyl alcohol and acetic acid.

It was also noted in the previous paper[1] that anhydrous acetic acid alone in benzene solution adds to vinylferrocene to give a high yield of α-ferrocenylethyl acetate. We have now prepared vinylruthenocene and vinylosmocene by methods analogous to that employed in the preparation of vinylferrocene and have found that absolute acetic acid adds to these olefins also. Addition, as with vinylferrocene, occurs in accordance with Markownikoff's rule, this fact being demonstrated by hydrolysis of the esters produced to the respective α-metallocenylethyl alcohols.

The rate of addition of absolute acetic acid to the vinylmetallocenes was followed spectrophotometrically. In the actual procedure, the disappearance of the characteristic absorption peaks in the ultraviolet or visible for the vinylmetallocenes was followed, no evidence having been found for the formation of any product other than the α-metallocenylethyl acetate. In all instances, a 1.5×10^{-3} molar solution of vinylmetallocene in absolute acetic acid was used; therefore, the rate constants obtained were for pseudo-first-order reactions. The results obtained are

Metallocene	$k \times 10^4$ sec.$^{-1}$ (40.0°)	Relative rate
Vinylferrocene	4.509 ± 0.069	1.00
Vinylruthenocene	5.371 ± .123	1.19
Vinylosmocene	20.83 ± .17	4.62

It is striking that the relative rates of addition of absolute acetic acid to the vinylmetallocenes closely parallel the rates of solvolysis of the corresponding α-metallocenylethyl acetates in aqueous acetone as determined by Richards and Hill.[7] These investigators have provided evidence that the solvolysis reactions proceed by way of the $B_{AL}1$ mechanism, with the following relative rates: α-ferrocenylethyl acetate, 1.00; α-ruthenocenylethyl acetate, 1.34; and α-osmocenylethyl acetate, 5.07. Inasmuch as the transition states for both the solvolysis reactions and the reactions involving addition of acetic acid to the vinylmetallocenes contain the α-metallocenyl carbonium ions as a component, it is reasonable that the relative rates be comparable.

In the addition of absolute acetic acid to the vinyl metallocenes, it is visualized that the transition carbonium ion is an unusually stable one owing to the overlap of the ha$_g$ molecular orbital[8] of the metallocene nucleus with the available *p*-orbital of the positively charged α-carbon atom. The observed order of the relative rates of addition can be attributed to increasing overlap as the size of the metal atom in the metallocene increases and, therefore, to increasing stabilization (ease of formation) of the carbonium ions. A similar concept has been invoked to explain the usual reactivity of a number of ferrocene derivatives in reactions proceeding through α-ferrocenylcarbonium ions.[7,9–12]

Experimental

Vinylferrocene was prepared by the method of Arimoto and Haven[5] from α-hydroxyethylferrocene. The material was purified by chromatography on Woelm (almost neutral) alumina of activity grade III,[13] Skellysolve B being used as eluent. The m.p. of the purified compound was 49–50° (reported[5] 48–49°).

α-Ruthenocenylethyl Alcohol.—A mixture of 8.3 g. (0.03 mole) of acetylruthenocene,[14] 1.4 g. of sodium borohydride, 50 ml. of methanol and 25 ml. of water was stirred overnight at room temperature. The excess of sodium borohydride was destroyed by the addition of 10 ml. of acetone, and the reaction mixture was extracted thoroughly with ether. The ether extract was dried over anhydrous sodium sulfate and the ether removed by distillation. The residue was chromatographed on activity grade IV alumina, Skellysolve B–ether being used as eluent. There was obtained 8.0 g. (96%) of colorless α-ruthenocenylethyl alcohol, m.p. 63–64°.

Anal. Calcd. for $C_{12}H_{14}ORu$: C, 52.23; H, 5.12; Ru, 37.86. Found[15]: C, 52.30; H, 5.32; Ru, 37.12.

Vinylruthenocene.—A solution of 5.0 g. (0.018 mole) of α-ruthenocenylethyl alcohol in the minimum amount of Skellysolve B was poured carefully into a 500-ml. suction flask which contained a 1-in. layer of activity grade I alumina. A balloon filled with nitrogen was attached to the side-arm of the flask, and the flask was stoppered and placed in an oil-bath maintained at 155° for 40 min. It was necessary to loosen the stopper several times to relieve the pressure inside the flask. After the mixture had been cooled to room temperature, it was transferred to a Soxhlet extraction apparatus. The mixture was extracted with Skellysolve B for 6 hr., the solvent evaporated by means of a rotary evaporator, and the residue chromatographed on activity grade I alumina, Skellysolve B being employed as eluent. The yield of vinylruthenocene was 2.3 g. (49%), m.p. 51–52°.

Anal. Calcd. for $C_{12}H_{12}Ru$: C, 55.88; H, 4.69; Ru, 39.43. Found: C, 55.90; H, 4.76; Ru, 39.65.

α-Osmocenylethyl Alcohol.—A mixture of 2.15 g. (0.0059 mole) of acetylosmocene,[14] 0.056 g. of sodium borohydride, 50 ml. of methanol and 25 ml. of water was stirred for 10 hr. at room temperature. Acetone then was added to decompose any unreacted sodium borohydride, and the reaction mixture was extracted thoroughly with benzene. The benzene extract was dried over anhydrous sodium sulfate and the benzene removed by distillation. The residue was chromatographed on activity grade V alumina, Skellysolve B–ether being used as eluent. There was obtained 1.61 g. (75%) of α-osmocenylethyl alcohol, m.p. 75.0–75.2°.

Vinylosmocene.—Into a 50-ml. round-bottom flask containing 5.0 g. of activity grade I Woelm non-alkaline (almost neutral) alumina was placed a solution of 0.2 g. (0.00058 mole) of α-osmocenylethyl alcohol in 3 ml. of an-

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(7) J. H. Richards and E. A. Hill, *J. Am. Chem. Soc.*, **81**, 3484 (1959).

(8) W. Moffitt, *ibid.*, **76**, 3386 (1954).

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(15) Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

hydrous benzene. The benzene was removed with the aid of a rotary evaporator by heating at 40° for 1 hr. *in vacuo*. The flask was flushed with nitrogen, stoppered, and rotated for 105 sec. in an oil-bath maintained at 160°. Upon removal from the oil-bath, the flask was immediately immersed in an ice-bath. The mixture was transferred to a Soxhlet extraction apparatus and extracted for 10 hr. with Skellysolve F. The extract was concentrated to a small volume by application of a jet of nitrogen and chromatographed on a column of activity grade III alumina, Skellysolve F being used as eluent. The yield was 0.095 g. (50%) of white crystalline vinylosmocene, m.p. 59–59.5°.

Anal. Calcd. for $C_{12}H_{12}Os$: C, 41.60; H, 3.49. Found: C, 41.70; H, 3.60.

Addition of Hydrogen Azide to Vinylferrocene in Benzene–Acetic Acid.—A mixture of 8.3 g. (0.039 mole) of vinylferrocene, 73 ml. of absolute acetic acid and 83 ml. of a 1.26 *N* solution of hydrogen azide (0.105 mole) in benzene was allowed to stand at room temperature for 3 days. The solvents were removed by means of a stream of nitrogen, and the residue was placed on an activity grade III alumina column from Skelly B solution. The first compound was eluted with Skelly B solvent and consisted of 3.6 g. (43%) of unconsumed vinylferrocene. Elution then with 90:10 Skellysolve B–chloroform afforded 1.0 g. (10%) of α-ferrocenylethyl azide, d. 1.347, $n^{20}D$ 1.6110.

Anal. Calcd. for $C_{12}H_{13}FeN_3$: C, 56.50; H, 5.14; N, 16.47. Found: C, 56.77; H, 5.01; N, 16.72.

Three additional compounds were eluted by use of Skellysolve B–chloroform (80:20). The infrared spectrum of the first of these (0.2 g.) contained an absorption peak at 5.81 μ, characteristic of the azido group. The identity of this compound is unknown, but it is probably 1,1′-di-(α-azidoethyl)-ferrocene.

Anal. Found: C, 51.05; H, 4.51; Fe, 19.93; N, 25.00.

The other two compounds consisted of 0.3 g. (3.4%) of acetylferrocene and 3.1 g. (34%) of α-ferrocenylethyl alcohol.

Reaction of Hydrogen Azide with α-Ferrocenylethyl Alcohol.—A mixture of 5.0 g. (0.022 mole) of α-ferrocenylethyl alcohol, 50 ml. of absolute acetic acid and 50 ml. of 1.26 *N* solution of hydrogen azide (0.063 mole) in benzene was allowed to stand at room temperature for 3 days. The solvents were removed by evaporation with the aid of a stream of nitrogen, and the residue was chromatographed on a column of activity grade III alumina, Skellysolve B–chloroform being used as eluent. Three compounds were eluted: 3.1 g. (57%) of α-ferrocenylethyl azide, 0.12 g. (2.4%) of acetylferrocene and 1.37 g. (34%) of unreacted α-ferrocenylethyl alcohol.

Reduction of α-Ferrocenylethyl Azide.—Into a Parr low pressure hydrogenation apparatus were placed 1.0 g. (0.0039 mole) of α-ferrocenylethyl azide, 0.1 g. of platinum oxide and 50 ml. of absolute methanol. After the vessel had been purged with hydrogen, the mixture was shaken for 2 hr. at room temperature under 4 atm. pressure of hydrogen. The mixture was filtered to remove the catalyst and the methanol was evaporated. The residual liquid was placed on a column of activity grade III alumina and chromatographed, chloroform being employed as eluent. There was obtained 0.7 g. (77%) of α-ferrocenylethylamine which was dissolved in anhydrous ethyl ether and treated with pure hydrogen chloride. The amine hydrochloride which precipitated was collected by filtration and recrystallized from methanol–benzene. The purified material had a m.p. of 166–167° (reported[6] 163–165°).

Preparation and Reduction of Ferrocenyl Methyl Ketoxime.—Into a Parr low pressure hydrogenation apparatus were placed 0.60 g. (0.0025 mole) of ferrocenyl methyl ketoxime, prepared by the method of Arimoto and Haven,[5] 30 ml. of absolute acetic acid and 0.1 g. of platinum oxide catalyst. Hydrogenation was effected for 3 hr. at room temperature under 60 lb./sq. in. pressure of hydrogen. The mixture was filtered, the solvent evaporated, and the amine converted to the hydrochloride as described above. The m.p. of the purified salt was 164–166°, also in admixture with the sample prepared from the azide.

Preparation of α-Ferrocenylethyl Acetate.—A mixture of 1.00 g. (0.0044 mole) of α-ferrocenylethyl alcohol, 5 ml. of pyridine and 2 ml. of acetic anhydride was allowed to stand overnight in a closed sublimation apparatus. The volatile components were then removed under reduced pressure, and the residue thus obtained was sublimed at 50° (bath temperature) and 0.1 mm. pressure. After further purification by resublimation, there was obtained 1.0 g. (85%) of yellow α-ferrocenylethyl acetate, m.p. 71–72° (reported[5] 67–68°).

Preparation of α-Ruthenocenylethyl Acetate.—A mixture of 1.00 g. (0.0036 mole) of α-ruthenocenylethyl alcohol, 5 ml. of pyridine and 2 ml. of acetic anhydride was allowed to stand at room temperature overnight. The reaction mixture was worked up as described above for the corresponding ferrocenyl compound. There was obtained 1.01 g. (88%) of white α-ruthenocenylethyl acetate, m.p. 61–62°.

Anal. Calcd. for $C_{14}H_{16}O_2Ru$: C, 52.88; H, 5.07; Ru, 31.98. Found: C, 53.15; H, 5.26; Ru, 31.83.

Preparation of α-Osmocenylethyl Acetate.—The same procedure was used as that employed for the preparation of α-ferrocenylethyl acetate. By this method, 0.6 g. (0.0017 mole) of α-osmocenylethyl alcohol was converted to 0.50 g. (75%) of α-osmocenylethyl acetate, m.p. 65.5–67.0°.

Anal. Calcd. for $C_{14}H_{16}O_2Os$: C, 41.38; H, 3.97. Found: C, 41.65; H, 4.23.

Addition of Absolute Acetic Acid to the Vinylmetallocenes.—A solution of 0.50 g. of the appropriate vinylmetallocene in 5 ml. of absolute acetic acid and 5 ml. of anhydrous benzene was allowed to stand at room temperature for 3 days. The solvents were removed *in vacuo* at a pot temperature of 50° and the residue was dried in a vacuum desiccator over potassium hydroxide. The material was then dissolved in chloroform and its infrared spectrum taken. In each case, the spectrum was essentially identical with that of the corresponding α-metallocenylethyl acetate. On chromatography of these materials on alumina, the α-metallocenylethyl alcohol invariably was isolated.

Procedure for Kinetic Measurements.—Pseudo-first-order rate constants for the addition of absolute acetic acid to the vinylmetallocenes were determined by following the decrease in intensities of characteristic absorption peaks of the vinylmetallocenes, a Beckman model DU spectrophotometer being employed. The cell compartment was maintained at a temperature of 40.0 ± 0.2°.

The wave lengths at which characteristic absorption peaks occurred in the ultraviolet or visible region were chosen as reference wave lengths for vinylferrocence and vinylruthenocene. Since the spectrum of vinylosmocene contained no well defined maximum in the usable range of the spectrophotometer, the wave length at which a 1.5×10^{-3} *M* solution of the compound in methanol exhibited an absorbance of 1.0 was chosen as the reference wave length. The various reference wave lengths employed were: vinylferrocene, 444 mμ; vinylruthenocene, 321 mμ; and vinylosmocene, 325 mμ.

Since the spectra of the products derived from vinylruthenocene and vinylosmocene (the α-metallocenylethyl acetates) exhibited no absorption maxima within the wave length range of the spectrophotometer, it was decided to follow the concentration changes of the vinylmetallocenes with the aid of a calibration curve. In each case, the curve was prepared in the following manner: (1) For a given concentration of vinylmetallocene in absolute acetic acid in the range of $0–1.5 \times 10^{-3}$ *M* absorbances were obtained for the appropriate wave length at various time intervals. (2) The same procedure was followed for the α-metallocenylethyl acetate. (3) The sums of the zero time absorbances for combinations of vinylmetallocene and corresponding acetate equal to a total concentration of 1.5×10^{-3} *M* were plotted *vs.* concentration of vinylmetallocene.

Kinetic determinations were carried out on 1.5×10^{-3} *M* solutions (initial concentration) of the vinylmetallocene in absolute acetic acid. These solutions were prepared by weighing the vinylmetallocene in a glass-stoppered bottle, adding the calculated amount of acetic acid from a 5-ml. buret and shaking the mixture vigorously for 30 sec. to obtain a homogeneous solution. Reaction times were calculated from the time that the acetic acid was added to the vinylmetallocene. Small portions of the solution were used to rinse the glass-stoppered 1-cm. silica absorption cell, and the cell was then filled with the solution. Duplicate absorbance readings were taken at convenient time intervals, depending upon the rate of the specific addition reaction. The average of these readings was used to determine the concentration of vinylmetallocene, and a plot made of log concn. *vs.* time. The slopes of these plots were used to determine the pseudo-first-order specific rate constants. Duplicate experiments were carried out in each case.[16]

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[16] The detailed kinetic data may be found in the Ph.D. thesis of G. R. Buell, University of Kansas, 1961.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS, LAWRENCE, KAN.]

Factors Affecting the Position of Alkylation of Alkali Metal Salts of Pyrrole with Allylic Type Halides[1]

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The reaction of alkali-metal salts of pyrrole with allyl, crotyl and benzyl halides affords a mixture of the 1- and 2-substituted pyrroles, along with varying amounts of disubstituted pyrroles. It has been found that the product ratio of the two monosubstituted pyrrole isomers in each case is affected markedly by the nature of the medium and of the metal ion. In general, the percentage of alkylation at the nitrogen atom (1-position) increases with the solvating power of the medium and decreases with the coördinating ability of the metal ion. These effects are explained on the basis that dissociation of the pyrryl–metal ion pair favors nitrogen alkylation. It has been shown that disubstituted pyrroles arise only from 2-alkylated pyrroles by further alkylation.

Introduction

The reaction of alkali metal salts of pyrrole with saturated alkyl halides, with few exceptions, has been reported to give nitrogen-substituted products.[2–8] Ciamician and Zanetti[9] reported that the reaction of pyrrylpotassium with an excess of refluxing methyl iodide gave only 1-methylpyrrole, but that increasing amounts of carbon-substituted product were formed when higher alkyl halides were used. For example, with an excess of refluxing amyl iodide, pyrrylpotassium afforded predominantly the carbon-substituted product,[10] a result which the authors attributed to the increase in reaction temperature brought about by substitution of amyl for methyl iodide. More recently, Cantor and VanderWerf[11] demonstrated that the reaction of pyrrylpotassium with allyl and with crotyl bromides in excess pyrrole–toluene gave preponderantly the corresponding 2-substituted pyrroles, a result more nearly to be expected for pyrrylmagnesium halides.[4,12,13] Treibs and Dietl[14] suggested that the position on the pyrryl anion resonance hybrid which makes the nucleophilic attack is determined by the ionic radius of the metal ion. Thus sodium and potassium salts (ionic radii of 0.98 for Na^+ and of 1.33 Å. for K^+) of pyrrole form predominantly nitrogen-alkylated products, whereas lithium and magnesium (each with an ionic radius of 0.78 Å.) salts give predominantly carbon-alkylated products. This suggestion is hardly adequate, however, to explain the varied behavior of pyrryl-metal salts in reaction with allylic halides.

Subsitution reactions involving a number of other ambident ions have been rather thoroughly studied in recent years. Zagorevsky found that carbon substitution in metal β-naphtholates increased with increasing reactivity of the halide[15] and decreasing electropositive character of the metal[16] used. He observed that use of the tetramethylammonium salt strongly favored alkylation at the oxygen atom. Curtin, Crawford and Wilhelm[17] reported that in the reaction of alkali metal salts of phenols, carbon alkylation was increased, at the expense of oxygen alkylation, by use of the following: non-polar solvents, salts of less acidic phenols, higher salt concentrations, salts of less electropositive alkali metals and more reactive halides (allylic rather than saturated halides). These data were explained on the basis of an earlier suggestion of Ingold,[18] that factors which increase dissociation of the phenolic salt favor ether formation and factors which increase ion aggregate formation favor dienone formation.

Kornblum[19] has pointed out, however, that the position of alkylation of the phenolic salts may depend to a large extent upon the degree of homogeneity or heterogeneity of the reaction mixture, carbon substitution being favored by heterogeneous conditions and oxygen alkylation by homogeneous conditions. More recently, Kornblum's group[20] has demonstrated that in such strongly solvating solvents as water, phenol and fluorinated alcohols considerable carbon alkylation of phenolic salts

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[1] This investigation was performed as a part of American Petroleum Institute Research Project 52 on "Nitrogen Constituents of Petroleum," which is conducted at the University of Kansas in Lawrence, Kan., and at the Bureau of Mines Experiment Stations in Laramie, Wyo., and Bartlesville, Okla.

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