# Novel Syntheses of Mesoionic Compounds and α-Amino Acid Derivatives from Acyltetracarbonylferrates

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**Abstract:** Acyltetracarbonylferrates [**1**, $R^1COFe(CO)_4^-$; $R^1$ = aryl] react with imidoyl chlorides [**2**, $R^2C(Cl) = NR^3$; $R^2$ = aryl; $R^3$ = aryl or alkyl] in methylene chloride at room temperature to give the mesoionic 1,3-oxazol-5-ones. The latter are convertible to α-amino acid derivatives under gentle conditions. The nature of $R^1$ and $R^2$ in **1** and **2**, respectively, has a significant influence on the reaction course. The formation of the mesoionic heterocycles is proposed to occur via iron-carbene complexes, formed by acyl transfer from the metal to nitrogen.

## Introduction

The application of metal carbonyls as reagents for organic synthesis is one of the most active areas of research in transition metal organometallic chemistry.[1,2] Several types of metal carbonyls have been investigated in considerable detail, including neutral and anionic metal carbonyls containing no other ligands. Simple metal carbonyl anions, as well as those which possess a cyclopentadienyl ligand, display a wide range of nucleophilicities.[3]

Of considerable promise, but less thoroughly studied, are acylmetal carbonyl anions. The organic chemistry of these anions has been covered in parts of several reviews, the most recent appearing in 1976[4] and 1977.[5] In addition, the preparations of α-diketones from acetals,[6] esters from Grignard reagents,[7] and ketones from halides[8] have been proposed to occur via anionic acylmetal carbonyl intermediates. It should be pointed out that such anions are also important precursors to various metal-carbene complexes.[9]

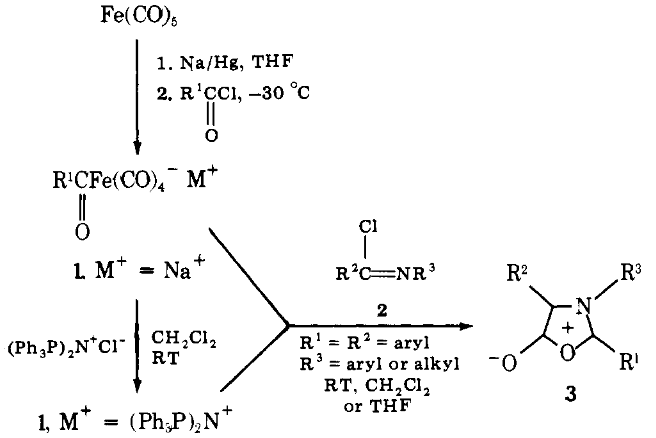
Imidoyl halides have proven to be useful in the development of new synthetic methodology,[10,11] particularly with reference to heterocyclic systems.[10-13] This paper describes the fascinating reaction of imidoyl chlorides with acyltetracarbonylferrates.

## Results and Discussion

The acyltetracarbonylferrate anion (**1**) was most conveniently generated by treatment of the cheap metal carbonyl, iron pentacarbonyl [$Fe(CO)_5$], first with sodium amalgam in tetrahydrofuran to generate disodium tetracarbonylferrate, and then reaction of the latter with the appropriate acid chloride at −30 °C. Either the sodium (**1**, M = $Na^+$) or bis(triphenylphosphine)iminium (**1**, M = $(Ph_3P)_2N^+$) acyltetracarbonylferrate[14]—formed by cation exchange of **1**, M = $Na^+$, with bis(triphenylphosphine)iminium chloride—was used for subsequent reactions.

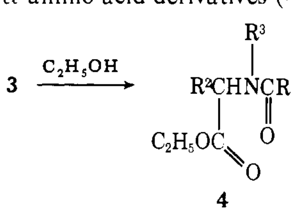
When benzoyl, *p*-methoxybenzoyl, or 2-furoyl tetracarbonylferrate (i.e., **1**, $R^1$ = aryl) was reacted with an equimolar amount of diaryl (**2**, $R^2$, $R^3$ = Ph, *p*-$ClC_6H_4$, *p*-$CH_3C_6H_4$, *p*-$BrC_6H_4$, *p*-$CH_3OC_6H_4$, 2-furyl, 2-thienyl) or aralkyl (i.e., $R^3 = CH_3$) imidoyl chlorides (**2**) in methylene chloride or THF under gentle conditions [room temperature, 1 atm ($N_2$)], mesoionic 1,3-oxazol-5-ones (**3**) were isolated in 37–65% yields. The yields of analytically pure products (crude yields were much higher), melting points, and elemental analyses for the 1,3-oxazol-5-ones are listed in Table I.

The mesoionic compounds were identified on the basis of analytical and spectral data [**3**, $R^1 = R^2$ = Ph; $R^3 = CH_3$, is a known compound).[15] A carbonyl stretching absorption for **3** was observed at 1700–1727 cm$^{-1}$ (KBr) in the infrared region (Table II), and molecular ion peaks were prominent in the mass spectra. Proton magnetic resonance spectra of **3** are also in accord with the assigned structure.

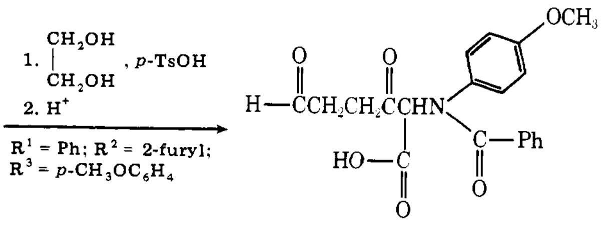


The reaction described above constitutes a simple, mild, and novel method for the synthesis of 1,3-oxazol-5-ones (**3**), an important class of mesoionic compounds.[16] In addition, this route enables one to obtain certain derivatives of **3** which are not easily accessible by other means.

These mesoionic compounds are exceedingly useful intermediates in their own right, providing an entry into a great variety of pharmacologically (and biologically) significant molecules, as well as compounds of theoretical interest (e.g., 10π-electron systems containing tetravalent sulfur atoms).[16] For example, numerous cycloaddition reactions are known, whereby 1,3-oxazol-5-ones react with unsaturated substrates (e.g., Schiff bases) to form new, important heterocycles (e.g., azetidinones, imidazoles, pyrroles).[16] Furthermore, exposure of **3** to alcohol (e.g., ethanol) at room temperature affords α-amino acid derivatives (**4**).[15] We obtained **4** in fine yields



**4**



**5**

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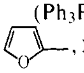
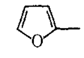
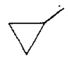
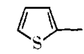
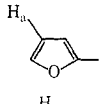
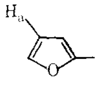
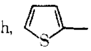
**Table I.** Products Obtained from Reaction of $R^1COFe(CO)_4^-$ (**1**) with $R^2C(Cl){=}NR^3$ (**2**)

| **1**, $R^1$ =, $M^+$ = | **2**, $R^2$ =, $R^3$ = | products | yield,[a] % | color[b] | mp,[c] °C | anal. found (calcd), % C | H | N |
|---|---|---|---|---|---|---|---|---|
| Ph, $(Ph_3P)_2N^+$ | Ph, $p$-$CH_3C_6H_4$ | **3** | 65 | Y | 199.5-202.0 | 80.44 (80.71) | 5.46 (5.23) | 3.85 (4.28) |
| Ph, $(Ph_3P)_2N^+$ | Ph, Ph | **3** | 61 | Y | 207.0-208.6 | 79.98 (80.49) | 4.48 (4.83) | 4.10 (4.47) |
| Ph, $Na^+$ | $p$-$BrC_6H_4$, Ph | **3** | 37 | Y | 128.0-132.5 | 64.54 (64.30) | 3.52 (3.60) | 3.45 (3.57) |
| Ph, $(Ph_3P)_2N^+$ | $p$-$BrC_6H_4$, Ph | **3** | 57 | | | | | |
| Ph, $(Ph_3P)_2N^+$ | Ph, $p$-$ClC_6H_4$ | **3** | 39 | Y | 180.6-182.4 | 72.78 (72.52) | 4.36 (4.06) | 3.94 (4.03) |
| Ph, $(Ph_3P)_2N^+$ | $p$-$CH_3OC_6H_4$, Ph | **3** | 53 | O | 172.0-175.4 | 76.52 (76.95) | 4.69 (4.99) | 3.74 (4.08) |
| Ph, $Na^+$ | Ph, $CH_3$ | **3** | 37[d] | YB | 147.5-148.2[e] | 76.85 (76.47) | 4.91 (5.22) | 5.09 (5.57) |
| $p$-$CH_3OC_6H_4$, $(Ph_3P)_2N^+$ | Ph, Ph | **3** | 61 | Y | 166.5-170.5 | 76.60 (76.95) | 5.40 (4.99) | 4.43 (4.08) |
| , $Na^+$ | Ph, $p$-$CH_3C_6H_4$ | **3** | 38 | YB | 167-171 | 75.49 (75.70) | 4.86 (4.76) | |
| Ph, $Na^+$ | , $p$-$CH_3OC_6H_4$ | **3** | 58 | OR | 165.8-168.0 | 72.02 (72.06) | 4.64 (4.54) | 4.31 (4.20) |
| $CH_3$, $Na^+$ | Ph, Ph | **6**<br>**7** | 25<br>34 | W<br>W | | | | |
| , $Na^+$ | Ph, Ph | **6**<br>**7** | 24<br>38 | W<br>W | 109.8-111.5[f] | | | |
| Ph, $Na^+$ | $C_2H_5$, Ph | **6**<br>**7** | 16<br>12 | W<br>W | <br>102.6-104.5[g] | | | |
| Ph, $Na^+$ | , $CH_3$ | **3** | 58 | Y | 149.5-151.0 | 65.57 (65.35) | 3.96 (4.31) | 5.42 (5.44) |

[a] Yields are of analytically pure products. [b] Y = yellow, O = orange, YB = yellow-brown, OR = orange-red, W = white. [c] Mesoionic compounds (**3**) melt with decomposition. All of the amides were identical with authentic samples prepared by different routes. [d] Byproducts obtained from workup of the reaction under oxidative conditions were $PhCOC(Ph){=}N(\rightarrow O)CH_3$ (18%) and $PhCON(CH_3)CH_2Ph$ (10%) (see Experimental Section). [e] Lit.[15] mp 151-152 °C dec. [f] Lit. mp 110-111 °C: R. J. DeFeo and L. V. Phillips, French Patent 1 393 657; *Chem. Abstr.*, **63**, 9680*a* (1965). [g] Lit. mp 103 °C: R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 4th ed., Wiley, New York, 1956, p 276.

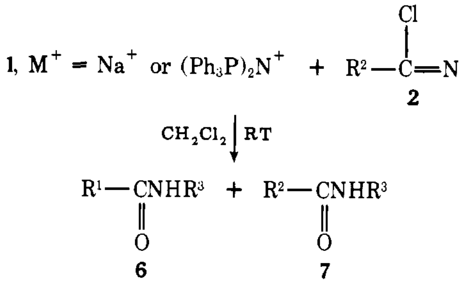
**Table II.** Pertinent Spectral Data for the 1,3-Oxazol-5-ones (**3**)

| **3**, $R^1$ =, $R^2$ =, $R^3$ = | IR, $\nu_{CO}$, $cm^{-1}$ [a] | $^1H$ NMR, $\delta$, ppm[b] | MS, $m/e$ |
|---|---|---|---|
| Ph, Ph, $p$-$CH_3C_6H_4$ | 1725 | 2.52 (s, 3 H, $CH_3$)<br>7.15-7.40 (m, 14 H, aromatic) | 327 |
| Ph, Ph, Ph | 1720 | 7.20-7.80 (m, 15 H) | 313 |
| Ph, $p$-$BrC_6H_4$, Ph | 1727 | 7.00-7.90 (m, 14 H) | |
| Ph, Ph, $p$-$ClC_6H_4$ | 1713 | 7.10-7.80 (m, 14 H) | |
| Ph, $p$-$CH_3OC_6H_4$, Ph | 1714 | | 343 |
| Ph, Ph, $CH_3$ | 1701 | 3.92 (s, 3 H, $CH_3$)<br>7.30-7.90 (m, 10 H, aromatic) | |
| $p$-$CH_3OC_6H_4$, Ph, Ph | 1715 | 3.70 (s, 3 H, $OCH_3$), 6.76 (d, 2 H, $J$ = 9 Hz, protons on carbons ortho to methoxy-bearing carbon), 6.9-7.8 (m, 12 H, other aromatic protons) | |
| , Ph, $p$-$CH_3C_6H_4$ | 1721 | 2.54 (s, 3 H, $CH_3$), 6.37 (m, 1 H, $H_a$), 7.05-7.50 (m, 11 H, other protons) | 317 |
| Ph, , $p$-$CH_3OC_6H_4$ | 1700 | 3.93 (s, 3 H, $OCH_3$), 6.40 (m, 1 H, $H_a$), 7.00-7.50 (m, 11 H, other protons) | 333 |
| Ph, , $CH_3$ | 1703 | 3.84 (s, 3 H, $CH_3$), 6.70-7.70 (m, 8 H, other protons) | 257 |

[a] KBr disk. [b] $CDCl_3$ with $Me_4Si$ as internal standard.

(e.g., $R^1 = R^2 = R^3$ = Ph, 80%; $R^1 = R^2$ = Ph, $R^3 = CH_3$, 80%; $R^1$ = Ph, $R^2$ = 2-thienyl, $R^3 = CH_3$, 87%). It is important to emphasize that **4** can be obtained directly from **1** and **2** without isolating the mesoionic compound **3**. An added feature in the case of $R^2$ = 2-furyl is the facile ring opening of the furan ring, under acidic conditions, to give the interesting polyfunctional amino acid **5**.[17] Also noteworthy for **4**, $R^2$ = 2-thienyl, is the well-known desulfurization of the thiophene unit thus affording aliphatic amino acid derivatives.[18]

Experiments carried out with $R^1$ or $R^2$ = alkyl demonstrate the remarkable sensitivity of the imidoyl chloride-acyltetracarbonylferrate reaction to the nature of these groups. When $PhC(Cl){=}NPh$ (**2**, $R^2 = R^3$ = Ph) was treated with **1**, $R^1$ = $CH_3$ or cyclopropyl, benzanilide (**7**) and the cross-coupled



$$\mathbf{1},\ M^+ = Na^+ \text{ or } (Ph_3P)_2N^+ + R^2C(Cl){=}NR^3\ (\mathbf{2}) \xrightarrow[\text{RT}]{CH_2Cl_2} R^1C(O)NHR^3\ (\mathbf{6}) + R^2C(O)NHR^3\ (\mathbf{7})$$

R¹ = alkyl; R², R³ = aryl
R¹ = R³ = aryl; R² = alkyl

amide **6** ($R^1$ = $CH_3$, $C_3H_5$; $R^3$ = Ph) were formed. Similar products were obtained from **1**, $R^1$ = Ph, and **2**, $R^2$ = $C_2H_5$; $R^3$ = Ph. 1,3-Oxazol-5-ones (**3**) were not detected in any of these reactions.

A possible mechanism for formation of 1,3-oxazol-5-ones (**3**) is outlined in Scheme I. Displacement of chloride from **2** by the acyltetracarbonylferrate ion would give **8**. What we believe occurs next is, to our knowledge, a rather unique acyl migration from iron to nitrogen affording a heteroatom stabilized carbene complex (**9a**). Structure **9b** would be expected to contribute significantly to the resonance hybrid of the carbene complex.[9] Ligand migration (**10**) and subsequent decomplexation would afford the amido ketene **11**, which is known[15,16] to cyclize to the 1,3-oxazol-5-one (**3**). The ligand migration step giving **10** is probably a facile one since the yield of **3** ($R^1$ = $R^2$ = Ph; $R^3$ = $p$-$CH_3C_6H_4$ (from **1** and **2**)) did not change when the reaction was effected in a carbon monoxide rather than nitrogen atmosphere.

The amide **7** may result from hydrolytic cleavage of the vinylmetallic complex **8**, while the cross-coupled amide **6** may arise by protonation, and subsequent hydrolysis, of **9b**. The aldehyde **12** should be a byproduct of the latter process, and **13** should be formed on decomplexation of **8**. When $CH_3CO$-$Fe(CO)_4^-$ was reacted with PhC(Cl)=NPh for a brief period of time (1-2 h), benzaldehyde (**12**, $R^2$ = Ph) was formed along with **6** and **7**. Similarly, in addition to **6** and **7**, benzaldehyde (**13**, $R^1$ = Ph) and propionaldehyde (**12**, $R^2$ = $C_2H_5$) were produced from the reaction of **1**, $R^1$ = Ph, with $C_2H_5C(Cl)$=NPh. Condensation and polymerization of the aldehydes occurred under the "usual" reaction conditions (i.e., 12-24 h).

Direct conversion of **8** to **10** may occur without the intermediacy of **9** (dotted lines in Scheme I).[19] However, it is then difficult to rationalize the formation of **12** in the reactions where $R^1$ or $R^2$ = alkyl in the reactants.

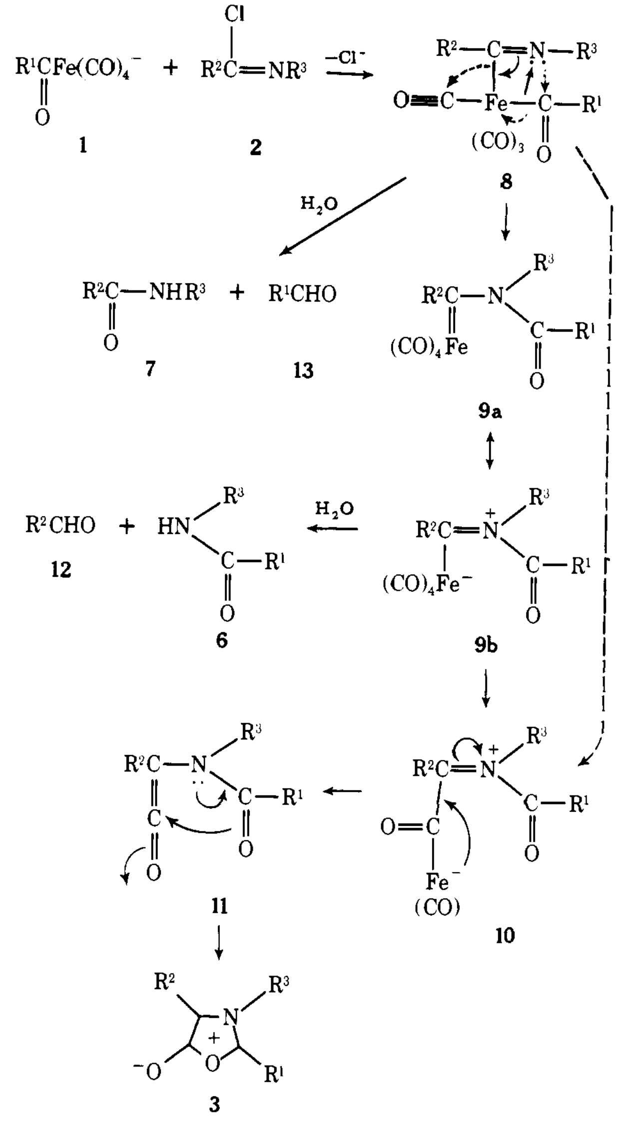
In summary, a novel synthesis of 1,3-oxazol-5-ones and α-amino acid derivatives occurs by treatment of imidoyl chlorides with the acyltetracarbonylferrate anion. This work demonstrates the importance of ligand migration processes, both common (involving CO)[20] and uncommon (involving COR¹), and how such processes can be applied in genuinely useful organic synthesis.

## Experimental Section

**General.** Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR20 A or a Unicam SP1100 spectrometer, each equipped with a calibration standard. Proton magnetic resonance spectra were determined on Varian T-60 and/or HA-100 spectrometers (tetramethylsilane was used as internal standard). Mass spectral determinations were made using a AEI MS902 spectrometer. Elemental analyses were performed by Butterworths Microanalytical Consultancy, Ltd., Teddington, England, and by M-H-W Laboratories, Phoenix, Ariz.

Iron pentacarbonyl was purchased from Pressure Chemical Co., and was used as received. Bis(triphenylphosphine)iminium chloride was synthesized according to the procedure of Ruff and Schlientz.[21]

**Scheme I**



The imidoyl chlorides (**2**) were generally prepared by the method of Braun and Pinkernelle.[22] Exceptions include $N$-$p$-methoxyphenyl-2-furimidoyl chloride (**2**, $R^2$ = 2-furyl; $R^3$ = $p$-$CH_3OC_6H_4$), mp 50.5-51.8 °C (lit.[23] mp 44-45 °C), prepared according to the procedure of Hahn and Grdinic, and $N$-phenylpropionimidoyl chloride (**2**, $R^2$ = $C_2H_5$; $R^3$ = Ph), synthesized by the method of Fujimoto and co-workers,[24] which was modified as follows. To an ice-cold tetrahydrofuran (150 mL)-pyridine (9 mL) solution of propionanilide (0.1 mol) was added, drop by drop, phosgene (10.7 mL, 0.15 mol) in benzene (20 mL). After overnight refrigeration of the resultant suspension, pyridine hydrochloride was filtered and washed twice with benzene (50 mL each), and the washings were added to the filtrate. The solvents were removed by rotary evaporation (ca. 30 Torr), and subsequent distillation gave 82% of **2**, $R^2$ = $C_2H_5$; $R^3$ = Ph, bp 47.0-49.0 °C (0.5 mm) [lit.[24] bp 55.0-56.0 °C (2.5 mm)].

Solvents were dried and purified by standard techniques. All reactions and manipulations were effected under a dry nitrogen atmosphere, unless otherwise noted.

**Reaction of Acyltetracarbonylferrates (1) with Imidoyl Chlorides (2).** Disodium tetracarbonylferrate (2.92 mmol), prepared by standard reduction of $Fe(CO)_5$ by Na/Hg,[8,14] in tetrahydrofuran (17.5 mL) was treated with an equivalent amount of an acid chloride in tetrahydrofuran (5.0 mL) at −30 °C and then warmed to room temperature with stirring (30 min). The generated **1**, M = $Na^+$, was then reacted with an imidoyl chloride; alternatively, **1**, $M^+$ = $Na^+$, was converted to **1**, $M^+$ = $(Ph_3P_2)N^+$, prior to reaction with **2** (Table I). This was effected by adding the suspension to a methylene chloride (17.5 mL) solution of bis(triphenylphosphine)iminium chloride (2.85 mmol). The reaction mixture was stirred at room temperature for 30 min and filtered (NaCl), the solid was washed with two 2-mL portions of $CH_2Cl_2$, and the washings were added to the filtrate. The residue obtained by filtrate evaporation was dissolved in 10 mL of $CH_2Cl_2$ or THF and treated with the imidoyl chloride (2.80 mmol). The reaction mixture, after being stirred at room temperature for 12–24 h, was worked up for the particular cases as follows.

**A ($R^1 = R^2 = R^3 = Ph$).** The reaction mixture was filtered and the yellow powder was washed twice with 4-mL portions of $CH_2Cl_2$ to give crude **3**. Concentration of the combined filtrate gave an additional small quantity of the 1,3-oxazol-5-one. Pure **3** was obtained as very thin, yellow needles by recrystallization of the crude materials from acetonitrile containing a small amount of acetic anhydride.

**B ($R^1 = R^2 = Ph$; $R^3 = p\text{-}CH_3C_6H_4$).** The reaction mixture was filtered and washed as described for A. Recrystallization from acetonitrile afforded a yellow, fibrous solid.

**C ($R^1 = R^3 = Ph$; $R^2 = p\text{-}BrC_6H_4$).** The dark brown reaction mixture was concentrated to ca. 4 mL and filtered, and the solid was washed three times with 2-mL portions of 1:1 $CH_2Cl_2$–ether. Analytically pure product was obtained by recrystallization from a minimum amount of $CH_2Cl_2$.

**D ($R^1 = R^2 = Ph$; $R^3 = p\text{-}ClC_6H_4$).** The reaction mixture was filtered, and the yellow powder was first washed with a small amount of $CH_2Cl_2$ and then with ether to give analytically pure **3**.

**E ($R^1 = R^3 = Ph$; $R^2 = p\text{-}CH_3OC_6H_4$).** The reaction mixture was worked up as described in D. Crude **3** was recrystallized from $CH_3CN$ containing a small amount of acetic anhydride to give orange-yellow crystals.

**F ($R^1 = p\text{-}CH_3OC_6H_4$; $R^2 = R^3 = Ph$).** The yellow solid, after filtration, was washed twice with 0.5 mL of $CH_2Cl_2$ and then with 3 mL of 1:1 $CH_2Cl_2$–ether to give pure **3**.

**G ($R^1 = R^2 = Ph$; $R^3 = CH_3$).** The reaction mixture was concentrated to ca. 5 mL, and 10 mL of $CH_2Cl_2$ was added. The resulting sodium chloride was removed by filtration and washed twice with 2 mL of $CH_2Cl_2$, and the combined filtrate and washings were concentrated to near dryness. Ether (10 mL) was added, and the mixture was filtered. The solid was washed with three 2.5-mL portions of ether to give crude **3** as an orange-brown powder. Recrystallization from 5 mL of acetonitrile–ether (1:1) containing a small amount of acetic anhydride gave pure **3** as yellow-brown crystals.

The combined filtrate and washings were treated with methanol (1.5 mL), exposed to air for several days, and filtered, and the filtrate was evaporated at ca. 30 Torr. The residue obtained from filtrate evaporation was chromatographed on silica gel. Elution with chloroform containing an increasing amount of ether gave the following, in order of elution.

(1) $PhCOC(Ph){=}N({\rightarrow}O)CH_3$: 18% yield; mp 98.0–98.8 °C; IR (KBr) $\nu_{CO}$ 1677, $\nu_{NO}$ 1310 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 3.55 (s, 3 H, $CH_3$), 7.20–7.70 (m, 10 H, aromatic); MS *m/e* 239 ($M^+$).

Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.33; H, 5.37; N, 5.67.

(2) **4**, $R^1 = R^2 = Ph$; $R^3 = CH_3$, 3% yield (the methanolysis product of **3**).

(3) $PhCON(CH_3)CH_2Ph$: 10% yield; IR (neat) $\nu_{CO}$ 1635 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 2.85 (s, 3 H, $CH_3$), 4.68 (s, 2 H, $CH_2$), 7.30, 7.38 (s, 10 H, aromatic protons). This product was identical with the compound obtained by reaction of *N*-methylbenzylamine with benzoyl chloride in a mixture of 2 N NaOH and benzene.

**H ($R^1$ = 2-Furyl; $R^2 = Ph$; $R^3 = p\text{-}CH_3C_6H_4$).** The reaction mixture was concentrated to half its original volume and 10 mL of $CH_2Cl_2$ was then added. The mixture was filtered and washed with 2 mL of $CH_2Cl_2$, and the combined filtrate and washings were concentrated in vacuo. The residue was redissolved in 4 mL of $CH_2Cl_2$, treated with 10 mL of hexane, and then refrigerated overnight. Filtration gave crude **3**, which was recrystallized from 12 mL of $CH_2Cl_2$–ether (1:2) to give yellow-brown crystals.

**I ($R^1 = Ph$; $R^2$ = 2-Furyl; $R^3 = p\text{-}CH_3OC_6H_4$).** The reaction mixture was concentrated to ca. 10 mL, and 10 mL of $CH_2Cl_2$ was added. The mixture was filtered, and the solid was washed until the washing was colorless. The combined filtrate and washings were concentrated until a precipitate appeared (ca. 5 mL). Addition of 3 mL of $CH_2Cl_2$ homogenized the mixture, and the resulting solution was treated with ether (12 mL) and then kept in a refrigerator until crude **3** precipitated out of solution. Recrystallization from 15 mL of $CH_2Cl_2$–ether (2:1) afforded pure **3** as bright orange-red crystals.

**J ($R^1 = Ph$; $R^2$ = 2-Thienyl; $R^3 = CH_3$).** The reaction mixture was worked up as described for I. Pure **3** was obtained on recrystallization from ether-acetonitrile (2.5/1.0).

**K ($R^1 = CH_3$; $R^2 = R^3 = Ph$).** The reaction mixture, which did not show any infrared bands characteristic of a 1,3-oxazol-5-one, was treated with 3 mL of methanol and then stirred for 2 days. The mixture was poured into $H_2O$ (20 mL) and then extracted with two 50-mL portions of ether. The combined ether extracts were washed with four 10-mL portions of $H_2O$, dried ($MgSO_4$), and concentrated. The resulting brown oil was dissolved in the minimum amount of ether, and hexane was then added until the solution became cloudy. After refrigeration, colorless crystals were isolated, consisting of a mixture of acetanilide and benzanilide. Separation of the latter mixture was achieved by using preparative thin layer chromatography (silica gel) with chloroform-ether (9:1). The mother liquor (above) contained **6** and **7**, which were separated in the same fashion. In addition, less than 10 mg of a third product was also isolated. It may be $PhCOCOCH_3$ [$^1H$ NMR $\delta$ ($CCl_4$) 2.83 ($CH_3$)], but it could not be obtained in an analytically pure state. No alcoholysis or hydrolysis product of the mesoionic 1,3-oxazol-5-one was detected. Acetanilide and benzanilide were shown to be identical with authentic samples.

**L ($R^1$ = Cyclopropyl; $R^2 = R^3 = Ph$).** The reaction mixture was concentrated (no 1,3-oxazol-5-one present), treated with 20 mL of $CH_2Cl_2$, and then filtered. After exposure of the filtrate to air, the solution was filtered again, and the filtrate was evaporated. The resulting brown semisolid was dissolved in the minimum amount of chloroform, hexane was added, and benzanilide (**7**) was precipitated on cooling of the solution. The filtrate was concentrated, and then preparative thin layer chromatography (see K) gave pure *N*-phenylcyclopropanecarbamide (**6**), as well as a small amount of benzanilide (**7**). Compounds **6** and **7** had identical properties with authentic materials.

**M ($R^1 = R^3 = Ph$; $R^2 = C_2H_5$).** The reaction mixture, which did not contain 1,3-oxazol-5-one, was treated with 3 mL of methanol and allowed to stand at room temperature for 5 days. The solution was treated with ether and then washed with $H_2O$, dried ($MgSO_4$), and concentrated to give a brown semisolid. Column chromatography on silica gel, with chloroform-ether, gave benzanilide (**6**) and propionanilide (**7**), each of which was recrystallized, and shown to be identical with authentic samples.

**General Procedure for Alcoholysis of 1,3-Oxazol-5-ones (3).** The mesoionic compound was treated either with excess alcohol (methanol, ethanol) at room temperature, followed by ether extraction,[15] or with commercial chloroform (i.e., containing approximately 1% ethanol) by Soxhlet extraction.

**4 ($R^1 = R^2 = Ph$; $R^3 = CH_3$)** was isolated in 80% yield, with properties in accord with those reported by Bayer et al.[15]

**4 ($R^1 = R^2 = R^3 = Ph$)** was obtained in 80% yield: mp 97.8–98.6 °C; IR (KBr) $\nu_{CO}$ 1738, 1639 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.26 (t, 3 H, $CH_3$, $J$ = 7.0 Hz), 4.30 (q, 2 H, $CH_2$), 6.29 (s, 1 H, CH), 6.90–7.25 (m, 15 H, aromatic); MS *m/e* 259 ($M^+$).

Anal. Calcd for $C_{23}H_{21}NO_3$: C, 76.86; H, 5.89; N, 3.90. Found: C, 77.33; H, 5.82; N, 3.72.

**4 ($R^1 = Ph$; $R^2$ = 2-Thienyl; $R^3 = CH_3$)** was obtained in 87% yield: mp 37.5–39.0 °C; IR (KBr) $\nu_{CO}$ 1735, 1640 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.19 (t, 3 H, $CH_3$, $J$ = 6.5 Hz), 2.88 (s, 3 H, $NCH_3$), 4.38 (q, 2 H, $CH_2$), 6.43 (s, 1 H, CH), 6.70–7.60 (m, 8 H, aromatic protons); MS *m/e* 303 ($M^+$).

Anal. Calcd for $C_{16}H_{17}NO_3S$: C, 63.34; H, 5.64; S, 10.57. Found: C, 63.31; H, 6.00; S, 10.39.

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# Polymeric Pseudocrown Ethers. 1. Synthesis and Complexation with Transition Metal Anions

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**Abstract:** Polymeric pseudocrown ethers (PPCE) are prepared by the reaction between chloromethylated styrene-divinylbenzene copolymers and polyoxyalkylene under Williamson ether-synthesis conditions. Synthetic aspects, the polymer selection, and reaction conditions are discussed. Effective PPCE synthesis is obtained with flexible polymers, and high cyclization yields are obtained, even when 3 molar excess of the diol is used. A detailed study of the coordination of transition metals, including $Au^{3+}$, $Fe^{3+}$, and $Zn^{2+}$, as chlorides, bromides, or iodides in HX and/or NaX solutions show that PPCE coordinate $MX_4^-$ or $MX_4^{2-}$ complexes (M = Au, Fe, Zn; X = Cl, Br, I) without competition from large excess of hydrogen or $X^-$ ions. The coordination patterns of the various PPCE show that coordination is most effective when the anions fit well in the PPCE cavity (whose dimensions were estimated from Corey-Pauling-Koltun models). The coordination of $MX_4^-$ or $MX_4^{2-}$ anions (ionic diameter 9–11 Å) is most effective with PPCE-14 (incorporating 14 oxygens, cavity diameter 10.5–13 Å) and falls off to zero with PPCE-4 (incorporating four oxygens).

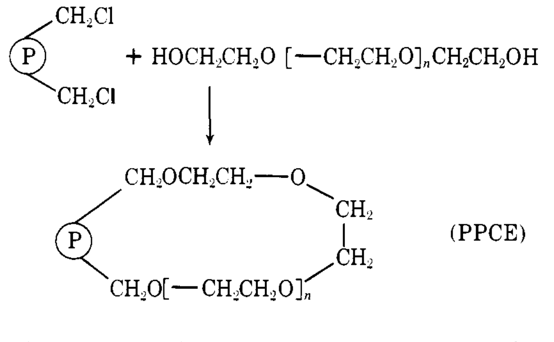
## I. Introduction

The synthetic work of Pedersen on macrocyclic ethers[1] has attracted the attention of many workers in various research areas. Major efforts have been directed toward the design and synthesis of ligands,[2] the correlation between ligand structure and transport phenomena in biosystems,[3] and the preparation of synthetic membranes.[4] The thermodynamics of cation-ligand interaction has been thoroughly studied,[5] and the feedback to organic chemistry in host-guest chemistry[6] and phase transfer catalysis[7] has been very significant.

Soluble polymers incorporating pendant crown-ether groups were synthesized by Smid and co-workers from 4′-vinylbenzo-15-crown-5 and 4′-vinylbenzo-18-crown-6 monomers,[8] and were found to be very similar to the monomers[9] in their cation complexation properties. In addition, owing to their good water solubility,[10] they bind organic solutes as picrate ions, methyl orange, phenolphthalein, as well as other organic neutral and anionic solutes.[10,11] Poly(vinylbenzo-18-crown-6) dissolved in water catalyzes the decarboxylation of 6-nitrobenzisoxazole 3-carboxylate by a factor of 2300.[12]

Fritz's report,[13] that a polymer incorporating pendant ester groups (Amberlite XAD-7) strongly binds gold as $AuCl_4^-$, followed with our studies on the coordination of thiocyanate complexes of platinum group metals,[14] suggested that metal ion coordination is accomplished by a cooperative effect of many ester groups and that the close proximity of the polymer backbone is not deleterious. This led us to assume that the synthesis of macrocyclic ethers incorporating a part of the macromolecular network would result in polymers of high coordinating power.

This work describes the synthesis of a range of such polymers described as "polymeric pseudocrown ethers" (PPCE),[32] prepared by the general scheme of eq 1.



(1)

(PPCE)

Anion complexation is an intriguing problem of similar importance to cation complexation. Graf and Lehn[15,16] have described anion inclusion by specially designed cryptates and Schmidtchen[17] has recently synthesized macrocyclic quaternary ammonium compounds.

This paper is concerned mainly with the synthesis of polymeric pseudocrown ethers and their coordination with anionic halide complexes of the transition metals. The complexation of acids[18] and $HFeCl_4$ complexation in phosphoric acid media[19] are presented in forthcoming papers in this series.

## II. Selection of Polymeric Precursors

The network structure of the polymer has an important role in the synthesis of polymeric pseudocrown ethers, as it has in the synthesis of other ion coordinating polymers.[21] Let us consider the various possibilities as described in Scheme I.

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