drogenation rate was low. Selectivity was not obtained; the product consisted of equal amounts of benzylamine and benzylmethylamine. As in the methyl isocyanide system, neither *tert*-butylamines nor methylcyclohexane were formed. The mixed isocyanide systems implicate the cluster as the primary catalyst or catalyst precursor.

We have tried to extend the catalytic hydrogenation to other molecules with triple bonds.[17] A hydrogenation of acetonitrile to ethylamine was achieved in a 90 °C homogeneous reaction of hydrogen and an acetonitrile solution of $Ni_4[CNC(CH_3)_3]_7$.[18] Reaction rate was very low and the products were $C_2H_5NH_2$ and $(CH_3)_3CNHCH_3$ in a 5:1 molar ratio, respectively. An alternative reaction system comprising hydrogen and an acetonitrile solution of $Ni_4[CNC(CH_3)_3]_4$-$[C_6H_5C{\equiv}CC_6H_5]_3$ yielded $C_6H_5CH{=}CHC_6H_5$ and $C_2H_5NH_2$; hydrogenation of the isocyanide ligand was not detected. The turnover rate for the amine was about one per hour at 63 °C but the system became visibly heterogeneous after 1 h.

The mechanisms of these catalytic hydrogenations of CN triple bonds are not defined. In the cluster, the unique bridging isocyanide ligands[7,9] may be more susceptible to hydrogenation than terminally bound isocyanide ligands, since the bond order of the CN bond is lower[19] for these bridging ligands.[20] Hence, the most active intermediate could be $Ni_4(CNR)_7$ or possibly $Ni_4(CNR)_6$[7] which is formed when the parent cluster is heated. Alternative mononuclear intermediates are $Ni(CNR)_4$, $Ni(CNR)_3$, and $Ni(CNR)_2$. Our results show that the first is not an active intermediate in the reaction with hydrogen. NMR studies have failed to give evidence of the two possible unsaturated nomonuclear complexes but UV data[21] implicate a species like $Ni(CNR)_3$.

Acknowledgment. We gratefully acknowledge support of this research by the Advanced Research Projects Agency, Cornell Materials Science Center, and by the National Science Foundation.

References and Notes

(1) E. L. Muetterties, *Science*, **196**, 839 (1977).
(2) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975).
(3) R. Ugo, *Catal. Rev.-Sci. Eng.*, **11**, 225 (1975).
(4) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **85**, 451 (1976).
(5) M. G. Thomas, B. F. Beier and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976).
(6) E. L. Muetterties and G. C. Demitras, *J. Am. Chem. Soc.*, **99**, 2796 (1977).
(7) M. G. Thomas, W. R. Pretzer, B. F. Beier, F. J. Hirsekorn, and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 743 (1977).
(8) The one exception is the hydrogenation of acetylenes.
(9) V. W. Day, R. O. Day, J. S. Kristoff, F. J. Hirsekorn, and E. L. Muetterties, *J. Am. Chem. Soc.*, **97**, 2571 (1975).
(10) M. G. Thomas, E. L. Muetterties, R. O. Day, and V. W. Day, *J. Am. Chem. Soc.*, **98**, 4645 (1976).
(11) This product resulted from a catalytic hydrogenation of the solvent toluene.
(12) The metal was generated in the reaction flask by the hydrogenation of Ni-(1,5-cyclooctadiene)₂.
(13) This system and analogous systems with other isocyanides were analyzed by gas chromatography, utilizing either a 10-ft copper column of 10% Carbowax 20M and 2% KOH on Gas-Chrom Q, or a 6-ft stainless steel column of Chromosorb 103. Reference samples of the secondary amines were prepared by literature methods. The cyclohexyl isocyanide system was additionally characterized by gas chromatographic mass spectroscopy.
(14) Materials balance checks were based on (1) measurement of the hydrogen uptake, (2) measurement of the amount of amine produced, and (3) the molar ratio of Ni₄(CNR)₇ to Ni(CNR)₄ determined by NMR analysis.
(15) A very small amount of solid formed in the late stages of the reaction, but no methylcyclohexane.
(16) The rate acceleration at substantially higher pressures has not been established yet. Experimental complications due to metal surface catalyzed decomposition of the nickel clusters and other related problems have not been resolved.
(17) In attempts to effect the hydrogenation of ¹⁵N₂ with Ni₄[CNC-(CH₃)₃]₄(C₆H₅C≡CC₆H₅)₃, very small amounts of ammonia were detected. However, we have never detected ¹⁵NH₃ in ¹⁵N₂ reactions, and, therefore, conclude that N₂ has not been the source of the NH₃ formed in the reactions. No ammonia was detected in a similar system with the Ni₄[CNC(CH₃)₃]₇ cluster at 90 °C.
(18) Attempts to isolate an Ni₄(CNR)ₓ(NCR)₇₋ₓ cluster have not been successful to date.
(19) Indicated from the infrared and x-ray (CN distance) data.
(20) Since there is a fast, intramolecular exchange of isocyanide ligands between terminal and bridging sites ($E_a \sim$ 16 kcal/mol), it could be argued that there is a small energy difference between the bridging and terminal bonding modes. Although this view may be reasonably accurate, it is possible that the difference in ligand bond energies could be relatively large if the nickel–nickel interactions were substantially different in the ground state and the intermediate or transition states for ligand intramolecular exchange.
(21) The complexes we have isolated in this (CH₃)₃CNC system are Ni(CNR)₄, Ni₄(CNR)₇, and Ni₄(CNR)₆. NMR studies of mixtures of Ni₄L₇ and NiL₄ show only the characteristic resonances of the two species below +60 °C (above which there is fast intermolecular ligand exchange). NMR studies of the reaction mixture from nickel(1,5-cyclooctadiene)₂ and RNC show, in addition to cyclooctadiene resonances, only the Ni₄L₇ and NiL₄ resonances in the reactant ratio range of RNC:Ni(COD)₂ of 7:4 to 4:1; at 4:1 and higher ratios only NiL₄ or the exchange singlet for NiL₄ + L was observed. UV studies of Ni(CNR)₄ show a departure from Beer's Law behavior at very low concentrations. Analogous UV studies of Ni(CNR)₄ + xCNR exhibited a similar departure at x = 5 and a conformance to Beer's Law at x = 100 (R = C(CH₃)₃). These data may reflect the equilibrium Ni(CNR)₄ ⇌ Ni(CNR)₃ + CNR since absorptions due to Ni₄(CNR)₇ could not be detected in the dilute Ni(CNR)₄ solution spectra at 20 °C. Very dilute solutions of Ni₄[CNC(CH₃)₃]₇ obeyed Beer's Law at 20 °C.

E. Band, W. R. Pretzer, M. G. Thomas, E. L. Muetterties*

Department of Chemistry
and Cornell Materials Science Center
Cornell University, Ithaca, New York 14853

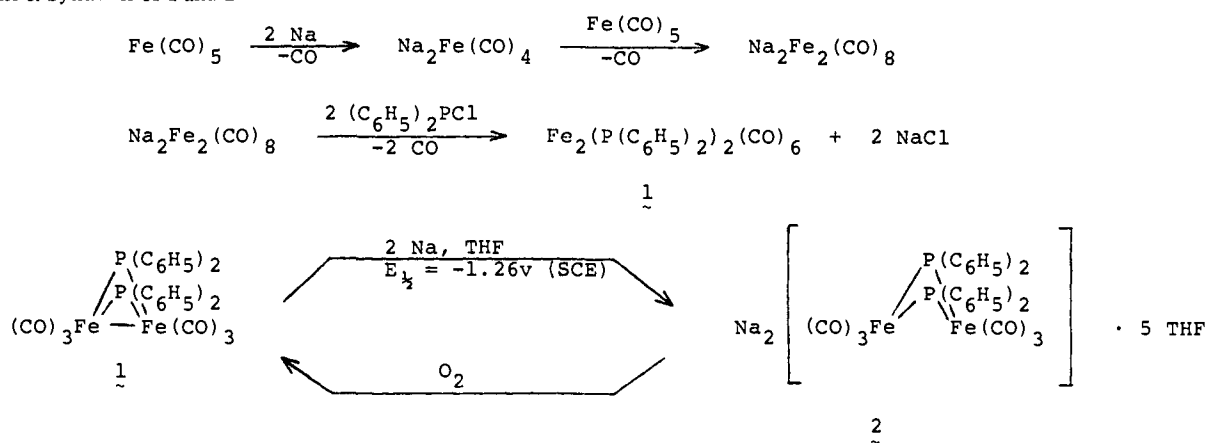## Metal Promoted Alkyl Migration in a Bimetallic Complex

Sir:

It is currently thought[1] that in selected cases transition metal cluster complexes may function as soluble analogues of heterogeneous catalysts. It is hoped that these cluster complexes will mimic the range of activity and reactions of heterogeneous catalysts, yet retain the selectivity and efficiency of homogeneous catalysts.

The key feature which distinguishes classic mononuclear homogeneous catalysts from heterogeneous or cluster catalysts is that the latter possess two or more adjacent metal sites. Novel modes of substrate–cluster binding and new reaction paths involving adjacent metals should prove central to the development of this field.

Oxidative addition[2] and alkyl migration[3] have been unifying concepts in the development of organo transition metal chemistry. Although pervasive in mononuclear systems, oxidative additions and alkyl migrations involving polynuclear complexes have been little studied.[4] In the case of clusters, the preparation of the reduced complexes which are required for the addition reaction is complicated by concurrent metal-metal bond cleavage and fragmentation.[5] Herein we report (i) the rational and efficient synthesis of a binuclear transition metal cluster complex, (ii) the reduction of the neutral parent cluster to the corresponding dianion, and (iii) the reaction of the dianion with alkylating agents affording *acyl* complexes via a novel metal-promoted alkyl migration.

Inasmuch as clusters are subject to reductive fragmentation, we have chosen to employ binuclear complexes containing bridging ligands. Di-μ-(diphenylphosphido)bis[tricarbonyliron(I)], $Fe_2[P(C_6H_5)_2]_2(CO)_6$ (**1**), was first prepared by Thompson[6] by reaction of iron pentacarbonyl with tetraphenyldiphosphine at 220 °C. We have developed an alternative synthesis which entails the addition of diphenylchlorophosphine to disodium octacarbonyldiferrate($-I$)[7,8] which is in turn derived from disodium tetracarbonylferrate($-II$)[7,9] and iron pentacarbonyl (Scheme I). The neutral dimeric complex **1** is isolated as orange plates in overall 60% yield

Scheme I. Synthesis of 1 and 2

$$Fe(CO)_5 \xrightarrow[-CO]{2 \text{ Na}} Na_2Fe(CO)_4 \xrightarrow[-CO]{Fe(CO)_5} Na_2Fe_2(CO)_8$$

$$Na_2Fe_2(CO)_8 \xrightarrow[-2\text{ CO}]{2 (C_6H_5)_2PCl} Fe_2(P(C_6H_5)_2)_2(CO)_6 + 2 \text{ NaCl}$$

$$\underset{\sim}{1}$$

Scheme II. Synthesis of Acyl Complexes 3

$$Fe_2(P(C_6H_5)_2)_2(CO)_6 + RLi$$

$$\underset{=}{1}$$
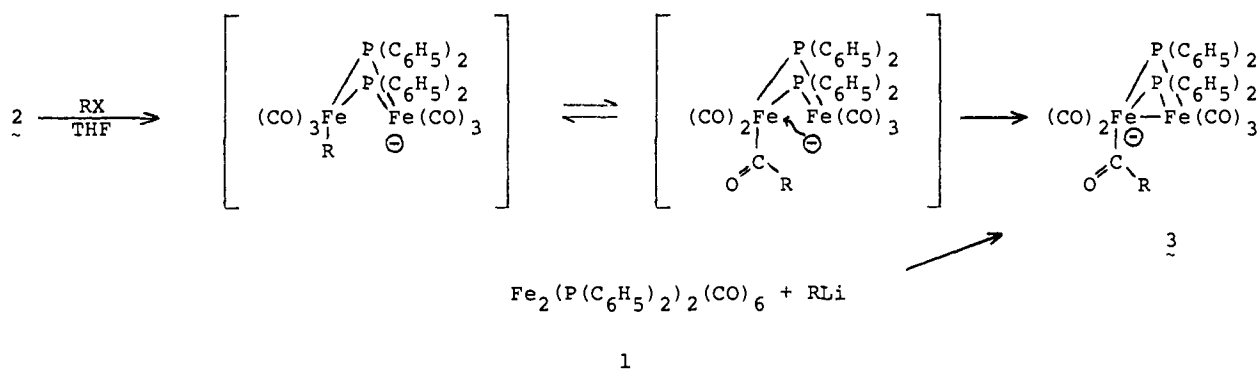
Table I. ^{13}C NMR Resonances

Complex	δ (MCO)	δ (MC(=O)R)	δ (CH₃)
NaCH₃Fe(CO)₄[a,b]	223.0[c]		−16.4
NaCH₃C(O)Fe(CO)₄[a,b]	220.5	277.2	51.8
3a (R = CH₃)[d]	221.7, 219.3	273.3	50.5

[a] Reference 16. [b] THF solution. [c] In parts per million from external TMS. [d] Me₂SO-d_6 solution.

(based on Fe(CO)₅). It is noteworthy that the entire reaction sequence may be carried out on a scale of tens of grams.

An x-ray diffraction study[10] of the parent complex **1** revealed two equivalent iron atoms, each bound to three terminal carbonyls and two bridging diphenylphosphido ligands. The presence of an iron-iron single bond is reflected in the Fe–Fe separation: 2.623 (2) Å.

The cyclic voltammogram[11a] of the parent complex **1** exhibits a single, two-electron, reversible reduction wave at −1.26 V (SCE) as described earlier.[11b] The dianion **2** is formed in >90% yield and isolated as red plates[12] upon reduction of the neutral dimer **1** with sodium dispersion in THF. Note that the dianion **2** formally contains no metal-metal bond. Exposure of the dianion **2** to dioxygen results in rapid, quantitative regeneration of the parent complex **1** (Scheme I).

Addition of *alkyl* halides and tosylates to the dianion **2** results in the formation of red, crystalline *acyl* complexes NaFe₂[P(C₆H₅)₂]₂(CO)₅[C(O)R]·2THF (**3**).[13,14] The generation of the acyl complex **3** is surely due to an oxidative addition of RX to the dianion **2** affording an intermediate[15] iron alkyl, followed by rapid rearrangement to the acyl **3** via alkyl migration (Scheme II). Complexes **3** exhibit acyl bands at 1560-1580 cm⁻¹ in addition to terminal carbonyl bands at 1995, 1940, 1905, and 1885 cm⁻¹. The ¹H NMR spectrum in

Me₂SO-d_6 of the acetyl complex **3a** (R = CH₃) shows a singlet at δ 2.25 (3 H). The ¹³C NMR spectrum of complex **3a** (Table I) is consistent with the acyl formulation. Preliminary data from single crystal x-ray diffraction studies of acyl complex **3a**[17] and LiFe₂[P(C₆H₅)₂]₂(CO)₅[C(O)C₆H₅]·3THF[18] indicate structures with an iron-iron single bond rather than coordination of the acyl oxygen[14] to the second metal atom.

Typically, the alkylation of mononuclear metal carbonyls affords metal alkyl, not acyl complexes.[19] Rearrangement of alkyls to acyls usually takes place in the presence of an external ligand. The mechanism[20] of such reactions normally involves a prior equilibrium in which migration of alkyl to CO yields an unsaturated acyl complex followed by rapid capture of the resulting site of unsaturation by an external ligand. We consider it likely that in this binuclear case the acyl is formed in the absence of an external ligand because the internal capture of the site of unsaturation occurs via the formation of a metal-metal bond (Scheme II).[21]

Protonation of the acyl complexes **3** affords aldehydes in quantitative yield together with the parent complex **1** and an isolable green-black microcrystalline solid **4**. Complex **4** is an iron carbonyl with CO stretching bands at 2024, 1993, 1960, and 1932 cm⁻¹. The presently ill-characterized **4**, which is expected to contain an Fe–Fe multiple bond, reacts with CO in THF at 1 atm to give the parent complex **1**. Few examples of additions of simple, two-electron donor ligands to a metal-metal multiple bond have been reported.[22]

We are currently examining the mechanism of the reaction leading to acyl complexes **3** as well as reactions of **3** with electrophiles, nucleophiles, and reducing agents. In addition, syntheses and reactions of clusters such as **4** are under investigation.

References and Notes

(1) (a) E. L. Muetterties, *Science*, **196**, 839 (1977), and references therein; (b) R. Ugo, *Catal. Rev.*, **11**, 225 (1975); (c) J. R. Norton, unpublished work. We thank Professor Norton for a preprint.

(2) (a) J. P. Collman, *Acc. Chem. Res.*, **1**, 136 (1968); (b) J. P. Collman and W. R. Roper, *Adv. Organomet. Chem.*, **7**, 54 (1968); (c) L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968); (d) J. Halpern, *Ibid.*, **3**, 386 (1970).

(3) (a) A. Wojcicki, *Adv. Organomet. Chem.*, **11**, 88 (1973); (b) A. Wojcicki, *ibid.*, **12**, 33 (1974); (c) F. Calderazzo, *Angew. Chem.*, **89**, 305 (1977), and references therein.

(4) For rare examples, see N. S. Lewis, K. R. Mann, J. G. Gordon, and H. B. Gray, *J. Am. Chem. Soc.*, **98**, 7461 (1976); N. E. Schore, C. Ilenda, and R. G. Bergman, *ibid.*, **98**, 7436 (1976); P. A. Wegner, V. A. Uski, R. P. Kiester, S. Debastani, and V. W. Day, *ibid.*, **99**, 4846 (1977).

(5) T. J. Meyer, *Prog. Inorg. Chem.*, **19**, 1 (1975).

(6) B. E. Job, R. A. N. McLean, and D. T. Thompson, *Chem. Commun.*, 895 (1966).

(7) R. G. Komoto, Ph.D. Thesis, Stanford University, Stanford, Calif., 1974.

(8) J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, and J. I. Brauman, *J. Am. Chem. Soc.*, **98**, 4685 (1976).

(9) Commercially available from Ventron Corporation, Alfa Products.

(10) L. F. Dahl, private communication.

(11) (a) A 0.2 M tetraethylammonium perchlorate solution in acetonitrile and a Hg electrode were employed. (b) R. E. Dessy, R. Kornmann, C. Smith, and R. Haytor, *J. Am. Chem. Soc.*, **90**, 2001 (1968).

(12) IR data: Fe–CO bands at 1930 (sh), 1905, 1845, 1825 (sh), and 1800 cm^{-1}. Anal. Calcd for $C_{50}H_{60}Fe_2Na_2O_{11}P_2$: C, 56.83; H, 5.72; Fe, 10.57; Na, 4.35; P, 5.86. Found: C, 56.66; H, 5.50; Fe, 10.77; Na, 4.32; P, 5.94.

(13) These complexes have been isolated and characterized by ^{1}H NMR and IR spectroscopy as well as elemental analysis. The lithium salts of acyl complexes **3** can be prepared by treating the parent complex **1** with 1 equiv of an alkyl or aryl lithium reagent.

(14) A few binuclear acyl complexes involving additional coordination of the acyl oxygen to the second metal center have previously been reported. See E. O. Fischer and V. Kiener, *J. Organomet. Chem.*, **23**, 215 (1970); P. F. Lindley and O. S. Mills, *J. Chem. Soc. A*, 1279 (1969); J. R. Blickensderfer, C. B. Knobler, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 2681, 2686 (1975).

(15) We have thus far been unable to detect these putative intermediate iron alkyl complexes, indicating that the subsequent alkyl migration occurs much more rapidly than the initial alkylation. This is true even in the case of benzylic substrates. Benzyl groups are generally sluggish to undergo alkyl migration.^{3}

(16) S. R. Winter, Ph.D. Thesis, Stanford University, Stanford, Calif., 1973.

(17) J. P. Collman, R. K. Rothrock, R. G. Finke, R. Ginsburg, and L. F. Dahl, unpublished work. Preliminary data: Fe–Fe = 2.66 (1) Å; Fe–O (acyl) = 3.76 (1) Å.

(18) J. P. Collman, R. K. Rothrock, R. G. Finke, W. H. Armstrong, J. M. Berg, M. A. Bobrik, A. M. Madonik, and K. O. Hodgson, unpublished work. Preliminary data: Fe–Fe = 2.670 (2) Å; Fe–O (acyl) = 3.678 (8) Å.

(19) For an exceptional case, see C. Cheng, B. D. Spivack, and R. Eisenberg, *J. Am. Chem. Soc.*, **99**, 3003 (1977); D. Forster, *ibid.*, **98**, 846 (1976).

(20) (a) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964); (b) K. Noack and F. Calderazzo, *J. Organomet. Chem.*, **10**, 101 (1967); (c) R. W. Glyde and R. J. Mawby, *Inorg. Chem.*, **10**, 854 (1971); (d) R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, **4**, 331 (1970).

(21) Although not known for mononuclear iron alkyls, there is a single report of an intermolecular metal promoted alkyl migration for CH$_3$Mn(CO)$_5$, a system in which alkyl migration is unusually facile. See C. P. Casey, C. R. Cyr, R. L. Anderson, and D. F. Marten, *J. Am. Chem. Soc.*, **97**, 3053 (1975).

(22) (a) D. S. Ginley and M. S. Wrighton, *J. Am. Chem. Soc.*, **97**, 3533 (1975); (b) R. J. Klingler, W. Butler, and M. D. Curtis, *ibid.*, **97**, 3535 (1975); (c) M. H. Chisholm, W. W. Reichert, F. A. Cotton, and C. A. Murillo, *ibid.*, **99**, 1652 (1977).

James P. Collman,* Richard K. Rothrock
Richard G. Finke, Francoise Rose-Munch
Department of Chemistry, Stanford University
Stanford, California, 94305
Received July 22, 1977

Conversion of the Carcinogen N-Acetoxy-2-acetamidofluorene to 4-Hydroxy-2-acetamidofluorene

Sir:

An erroneous observation has led to the discovery of a novel substitution reaction between water and the carcinogen N-acetoxy-2-acetamidofluorene (N,O-diacetyl-N-(2-fluorenyl)hydroxylamine, **1**). Gutmann et al. have reported that the principal product (60% of starting material) from solution of **1** in 0.14 M saline containing 0.01 M phosphate (pH 7.4) is 1-acetoxy-2-acetamidofluorene.[1] This conclusion was based solely on retention time of the unknown product on a high pressure liquid chromatography column, and contradicted earlier studies on reactions of **1**. In that earlier work,[2] the rate of formation of water-soluble radioactivity from N-CH$_3$^{14}CO$_2$-N-arylacetamide was determined. Release of radioactivity from labeled **1** was a pseudo-first-order reaction, and in 40% acetone the reaction was followed to the point of 60% release of radioactivity, with no indication that the reaction would stop short of 100% release. Because of the discrepancy between this result and that of Gutmann et al., it seemed likely that the principal product observed in the later work was a new substance, which fortuitously had the same retention time as the standard 1-acetoxy-2-acetamidofluorene. I now show that virtually no rearrangement takes place under the conditions described by Gutmann et al. and that the major product reported by that group is actually 4-hydroxy-2-acetamidofluorene (N-(4-hydroxy-2-fluorenyl)acetamide).

N-CH$_3$^{14}CO$_2$-2-acetamidofluorene was prepared by acetylating 435 mg of N-hydroxy-2-acetamidofluorene with 185 mg of labeled acetic anhydride in 5 mL of pyridine cooled in ice. After the reagents were mixed, the reaction was allowed to stand at room temperature for 1 h and was then precipitated into ice water. The precipitate was centrifuged, washed twice with ice water by mixing and recentrifugation, filtered on a glass frit, again washed, and dried overnight over CaCl$_2$ under vacuum; 427 mg (84%) of product was obtained, which was radiochemically homogeneous (TLC, silica gel, 5% ethyl acetate in benzene) and had a specific activity of 1.08 × 10^5 dpm/mg. This material (1.5 mg) was dissolved in acetone and added to the buffer described by Gutmann et al. (1 mL of acetone + 100 mL of buffer; 5 mL of acetone + 500 mL of buffer). After 2 h at 37 °C, 1-mL samples were removed for counting, the mixtures were extracted with ether, the remaining aqueous phase and the combined ether extracts (for each reaction) were again sampled, the ether was evaporated under reduced pressure, and the residues were chromatographed on silica gel thin layer plates. The residue from the first study was applied as a stripe 2.5 cm wide, developed with 5% ethyl acetate in benzene, the chromatogram was scanned on a radiochromatogram scanner, and all of the distinct UV-visible bands were scraped into test tubes and eluted with 95% ethanol. Samples were then assayed by ultraviolet spectrophotometry and liquid scintillation counting. The major product had an R_F very close to that of authentic 1-acetoxy-2-acetamidofluorene. However, <10% of the total radioactivity was recovered in the ether extract. After chromatography, the total recovery of radioactivity dropped to ~1%. The apparent specific activity (cpm/mL/A_{280}) of the major product was 2% of that of the starting material, demonstrating clearly that this compound was not a rearrangement product. The residue from the second study was applied as a spot to a corner of a preparative TLC plate, then chromatographed in two directions in the usual solvent. The spots were eluted and assayed as before. Following this procedure, virtually all radioactivity was removed from the detectable products. Thus, it was established that rearrangement of **1** is an insignificant reaction in aqueous medium at moderate temperature. It now remained to determine the identity of the major product.

Easily handled quantities of the unknown (**2**) were obtained by adding five 100-mg portions of **1** in 40 mL of acetone to 4 L of buffer at 37 °C and extracting the mixture with ether at least 2 h after each addition and before the next addition. This process was necessary because higher concentrations of **1** or its solvolysis products led to competing reactions which reduced the yield of **2**. The combined extracts were evaporated, and the residue was chromatographed on a column of silica gel eluted