Reactions of Aniline with Olefins Catalyzed by Group 8 Metal Complexes: N-Alkylation and Heterocycle Formation

Sir:

During our studies of the reactions of amines with olefins, we observed a novel and potentially very useful reaction of aniline with ethylene to yield a mixture of *N*-ethylaniline and 2-methylquinoline catalyzed by group 8 metal complexes. To our knowledge this observation is unique since it represents the first example of primary amine alkylation by olefins catalyzed by transition metal complexes[1] and also the first demonstration of a transition metal catalyzed heterocycle formation directly from aniline and ethylene. Herein we report our preliminary results in this area.

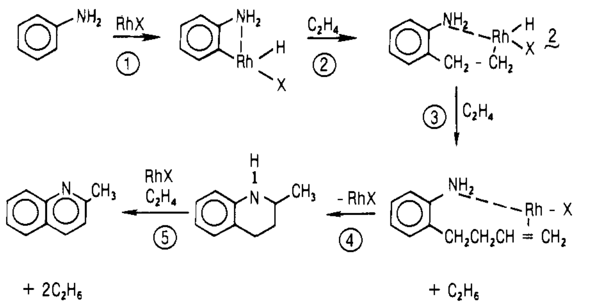
In a typical reaction, distilled and degassed aniline (100 mmol), $RhCl_3 \cdot 3H_2O$ (0.25 mmol) and triphenylphosphine (0.5 mmol) are loaded into a glass-lined autoclave under argon. The autoclave is pressurized to ~100 atm and heated to 200 °C. The reaction mixture becomes a reddish homogeneous solution. After 72 h, 30 turnovers (relative to the metal) of *N*-ethylaniline and 10 turnovers of 2-methylquinoline are obtained. The products were isolated by preparative liquid chromatography and their identity was established by comparison of mass spectral, ^{1}H and ^{13}C NMR, IR, and gas chromatographic data with those of authentic samples. Analysis of the gases by gas chromatographic-mass spectral techniques revealed the presence of considerable amounts of ethane and butenes. In the course of the reaction, rhodium(III) appears to be reduced to rhodium(I).[2]

Preliminary results indicate that the ratio of *N*-ethylaniline to 2-methylquinoline may be varied by changes in either the reaction conditions or in the group 8 metal complex. Thus, at lower ethylene pressures (10 atm) and temperature (150 °C), the same reaction produces 30 turnovers of *N*-ethylaniline and <1 turnover of 2-methylquinoline. Alternatively, catalysis by $PdCl_2$ (100 atm, 200 °C) leads predominantly to 2-methylquinoline (20 turnovers) while *N*-ethylaniline is the minor product (10 turnovers). Preliminary results suggest that this chemistry can be extended to propylene also.

Under the reaction conditions described above, *N*-ethylaniline reacts extremely slowly to produce very small quantities of *N,N*-diethylaniline. In addition, 1-butene does not react with aniline and butadiene gives only traces of heterocyclic products.[3] These results strongly suggest that (1) the alkylation of aniline and the heterocycle formation proceed by two independent pathways;[4] (2) the four carbons necessary for formation of 2-methylquinoline are not derived from butene (the product of ethylene dimerization) or butadiene; and (3) the formation of the heterocycle is not initiated by alkylation of the amino group of aniline, but most probably by alkylation of the aromatic ring (Scheme I).

In an attempt to shed light on the reaction path leading to 2-methylquinoline, we have taken advantage of the chemistry of hydridotris(triphenylphosphine)rhodium(I) (**1**).[5] This complex was found to be an inefficient catalyst for amine alkylation. Therefore, it enabled us to elucidate what we believe to be the mechanism of the heterocycle formation. Thus, heating aniline with ethylene at 150 °C for 96 h in the presence of **1** yielded 5 turnovers of 2-ethylaniline (Scheme I, steps 1 and 2). The identity of 2-ethylaniline was confirmed by gas chromatographic and mass spectral data. This reaction itself is remarkable in that it most certainly involves an ortho metalation of aniline, a reaction observed only once previously employing an osmium carbonyl cluster.[6]

Scheme I



The main side reaction in this system is the dimerization of ethylene to butenes. Therefore, it is expected that intermediate **2** (Scheme I) will have a tendency to insert a second molecule of ethylene to form an *o*-butenylaniline derivative (Scheme I, step 3). An intermediate analogous to **2** can be formed from 2-vinylaniline and a rhodium(I) hydride. Indeed, in the presence of catalytic quantities of **1** and ethylene (10 atm, 150 °C in dioxane), >90% of 2-vinylaniline[7] was converted to products.[8] The main component is the expected mixture of *cis*- and *trans*-2-(1-butenyl)aniline. Small amounts of indole (product of 2-vinylaniline cyclization) and 1,2,3,4-tetrahydro-2-methylquinoline are also present. The mixture of butenylanilines was separated by preparative gas chromatography and their structures were confirmed by mass spectral, NMR, and IR data. The identities of 1,2,3,4-tetrahydro-2-methylquinoline and indole were established by comparison of gas chromatographic and mass spectral data with those of authentic samples.

It should be noted that **1** is a very effective olefin isomerization catalyst.[9] Therefore, isomerization of 2-(3-butenyl)aniline (the expected primary product of 2-vinylaniline telomerization with ethylene) results in the formation of the thermodynamically stable product, 2-(1-butenyl)aniline, which was ultimately isolated. However, if an efficient amination catalyst is present, the cyclization to produce heterocycle is evidently preferred over isomerization.

The proposed cyclization of 2-(3-butenyl)aniline (Scheme I, step 4) is an intramolecular analogue of aniline alkylation by an olefin.[10] The feasibility of this type of cyclization is further supported by the recently reported intramolecular cyclization of 2-allylanilines to indole and quinoline derivatives assisted by palladium chloride.[11]

The last step, hydrogen transfer from 1,2,3,4-tetrahydro-2-methylquinoline to ethylene (Scheme I, step 5) has been experimentally demonstrated under conditions comparable to those used in the over-all reaction.[12] Thus, the results outlined in Scheme I strongly support the assumption that the observed heterocycle formation is a unique sequence of five consecutive steps catalyzed by group 8 metal complexes.

In summary, the findings described in this report are significant since they represent the first example of a transition metal catalyzed alkylation of a primary amine by olefins, and also offer the possibility for the formation of heterocyclic compounds directly from aniline and olefins. Presently, work is underway to further elucidate the mechanism of this heterocycle formation and to determine the scope and limitations of this and similar reactions.

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References and Notes

(1) Group 8 metal catalyzed homogeneous alkylation of amines has been limited to ethylene and secondary aliphatic or cyclic amines: D. R. Coulson, *Tetrahedron Lett.*, 429 (1971).

(2) Rhodium(III) is known to be reduced to rhodium(I) under similar conditions:

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R. Cramer, *J. Am. Chem. Soc.*, **87**, 4717 (1965); T. Alderson, E. L. Jenner and R. V. Lindsey, ibid., **87**, 5638 (1965); R. Cramer, *Acc. Chem. Res.*, **1**, 186 (1968).

(3) Aniline and butadiene are known to form mixtures of (*N*-phenyl)aminobutenes in the presence of catalytic quantities of Ni, Pd, Co, Rh, and Ir: S. Takahashi, T. Shibano, and N. Hagihara, *Bull. Chem. Soc. Jpn.*, **41**, 454 (1968); R. Baker, D. E. Halliday, and T. N. Smith, *Chem. Commun.*, 1583 (1971); R. Baker, A. H. Cook, D. E. Halliday, and T. N. Smith, *J. Chem. Soc., Perkin Trans. 2*, 1511 (1974); R. Baker, A. Onions, R. J. Popplestone, and T. N. Smith, *ibid.*, 1133 (1975).

(4) The mechanism of the alkylation most probably involves nucleophilic displacement of chloride by aniline to form a rhodium(I) anilide catalyst. The anilide may then attack coordinated olefin to produce an alkylanilide which can be protonated by additional aniline to regenerate the catalyst and liberate *N*-alkylaniline.

(5) Hydridotris(triphenylphosphine)rhodium(I) was recently characterized by an X-ray crystal structure determination and studied by ^{31}P NMR and a new synthetic route has also made it readily available in pure form: S. E. Diamond and F. Mares, *J. Organomet. Chem.*, **142**, C55 (1977); S. H. Strauss, S. E. Diamond, F. Mares, and D. F. Schriver, *Inorg. Chem.*, **17**, 3064 (1978).

(6) A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, **90**, 909 (1968); J. Dehand and M. Pfeffer, *Coord. Chem. Rev.*, **18**, 327 (1976); C. C. Yin and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1013 (1974).

(7) S. Sabetay, J. Bleger, and Y. de Lestrange, *Bull. Soc. Chim. Fr.*, **49**, 3 (1931).

(8) The telomerization of 2-vinylaniline and ethylene is not catalyzed by chlorotris(triphenylphosphine)rhodium(I). This fact strongly suggests that formation of intermediate **2** is necessary.

(9) C. J. Attridge and S. J. Maddock, *J. Chem. Soc. C*, 2999 (1971); J. Blum and Y. Becker, *J. Chem. Soc., Perkin Trans. 2*, 982 (1972).

(10) The synthesis of 2-(3-butenyl)aniline is underway; the study of its cyclization will be undertaken in the near future.

(11) L. S. Hegedus, G. F. Allen, and E. L. Waterman, *J. Am. Chem. Soc.*, **98**, 2674 (1976).

(12) Similar hydrogen-transfer reactions have been observed previously: T. Nishiguchi, K. Tachi, and K. Fukuzumi, *J. Org. Chem.*, **40**, 237 (1975).

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Polyoxomolybdate-Hydrocarbon Interactions. Synthesis and Structure of the $CH_2Mo_4O_{15}H^{3-}$ Anion and Related Methylenedioxymolybdates

Sir:

In light of the pronounced heterogeneous reactivity of molybdenum, tungsten, and vanadium oxides toward hydrocarbons,[1] it is somewhat surprising that no polyoxoanion clusters of these metals are known which contain hydrocarbon moieties bound to their surface oxygens. A recent study of the cobalt molybdate catalyzed selective oxidation of propylene to acrolein has provided evidence indicating that the rate-determining step is desorption of acrolein from the oxide catalyst surface.[2] As a logical starting point for the structural investigation of polyoxoanion-hydrocarbon interactions, we have therefore examined the solution reactivity of acrolein and other aldehydes toward polyoxomolybdates. We report here the isolation and characterization of several presumably isostructural $RCHMo_4O_{15}H^{3-}$ anions (R = C_2H_3, H, CH_3, C_6H_5, and CF_3), which contain RCH units bonded to the oxide surface of a tetranuclear polyoxomolybdate cluster.

Reaction of a large excess of acrolein with $[(n\text{-}C_4H_9)_4N]_2Mo_2O_7$[3] in hydrated CH_3CN-CH_2Cl_2 solution at 0 °C, followed by addition of ether, results in the formation of a precipitate which analyzes[4] as $[(n\text{-}C_4H_9)_4N]_3C_3H_4Mo_4O_{15}H$ (**1**) after purification by reprecipitation from CH_2Cl_2 with ether at 0 °C. Since attempts to obtain compound **1** in crystalline form have been unsuccessful owing to its instability in solution,[5] the structure of **1** has been inferred from a more stable analogue, the formaldehyde adduct $[(n\text{-}C_4H_9)_4N]_3CH_2Mo_4O_{15}H$ (**2**),[6] which is easily recrystallized from CH_2Cl_2-$C_6H_5CH_3$. Compounds **1** and **2** are assumed to contain isostructural anions since their IR spectra display several common features: a sharp OH absorption in the 3600-3650-cm^{-1} region, two C-O absorptions[7] in the 990-1100-cm^{-1} region, and an identical pattern of Mo-O absorptions in the 550-950-cm^{-1} region.

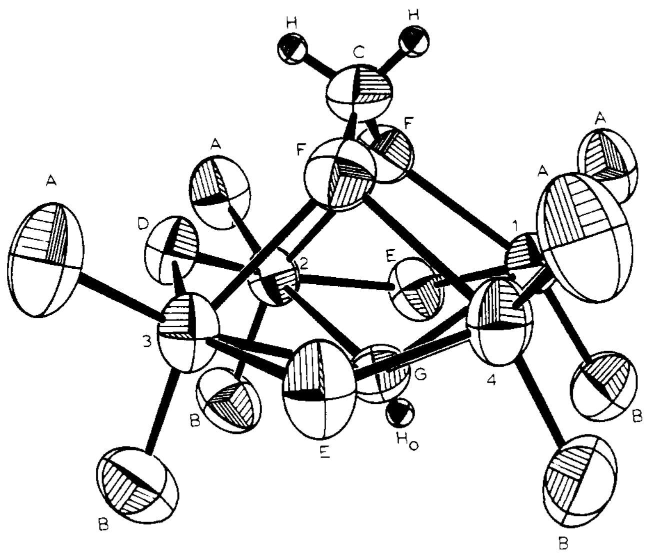

Figure 1. ORTEP drawing of the $CH_2Mo_4O_{15}H^{3-}$ anion as observed in single crystals of its $(n\text{-}C_4H_9)_4N^+$ salt. All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density; the three hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity. Molybdenum atoms are labeled with numbers and the 15 oxygen atoms are labeled according to the following scheme: A or B for the eight terminally bonded oxygens, D or E for the four doubly bridging oxygens, F for the two triply bridging oxygens, and G for the one hydroxyl oxygen. The carbon atom is designated by C and the hydrogen atoms by H's. The second doubly bridging O_D atom is hidden from view. The anion approximates C_{2v} site symmetry with C, O_G, and H_O ideally lying on the C_2 axis.

Table I. Average Molybdenum-Oxygen Distances for the $CH_2Mo_4O_{15}H^{3-}$ ion in $[(n\text{-}C_4H_9)_4N]_3CH_2Mo_4O_{15}H$

type[a]	distance,[b] Å
Mo-O_A Mo-O_B	1.702 (5, 5, 16, 8)
Mo-O_D	1.905 (5, 4, 4, 4)
Mo-O_E	1.924 (5, 3, 5, 4)
Mo-O_F	2.194 (5, 5, 9, 4)
Mo-O_G	2.456 (5, 24, 34, 4)

[a] See Figure 1 for labeling scheme. [b] For explanation of numbers in parantheses, see ref 11.

A single-crystal X-ray diffraction study[8] of **2** reveals that the compound contains discrete $CH_2Mo_4O_{15}H^{3-}$ anions (see Figure 1) which are structurally similar to the $(CH_3)_2AsMo_4O_{15}H^{2-}$ anion.[9] Although the anion possesses no rigorous crystallographic symmetry, it approximates rather closely C_{2v} site symmetry with all four molybdenum atoms coplanar to within 0.004 Å. As an indication of the extent to which chemical and structural analogies might exist between polyoxoanion clusters such as $CH_2Mo_4O_{15}H^{3-}$ and solid oxide bound hydrocarbons, we note that the oxygen atoms are in the polyoxoanion approximate a hexagonal close-packed arrangement. Each A layer would ideally contain two O_A, two O_B, and an adjacent O_D atom while the B layer would correspond to the pseudomirror plane which passes through the two O_E, two O_F, and the O_G atoms. The $CH_2Mo_4O_{15}H^{3-}$ anion can thus be described as having CH_2 and H units bonded to opposite side surfaces of a close-packed oxygen array in which molybdenum atoms occupy octahedral interstices. Consideration of bonding interactions (see Table I), however, produces a different description where $H_2CO_2^{2-}$ and OH^- groups are

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