by RPHPLC.[20] The yield of **5** based on fragment **1** was 59%. We have purified ca. 1 g of fragment **5** by RPHPLC.

The C-terminal five amino acids of the βA4 protein were coupled on the Merrifield resin in a stepwise manner.[24] Sequential couplings of fragments **2–4** were performed using our standard conditions (1.2–1.5 equiv of fragment, BOP activation, 23 °C)[13] in yields of >95%, 70–90%, and 80–90%, respectively.[25] The coupling of **5** to the resin-bound 25-mer β(18–42)′-Ⓡ was accomplished in 55–85% yield via four successive room-temperature coupling reactions, each using a progressively smaller amount of fragment **5** (2.3 equiv total) (coupling of the protected 25-mer β(1–25)′[13] to β(26–42)′-Ⓡ was unsuccessful). This final coupling is the only one in the synthesis in which epimerization at the C-terminus of the soluble fragment is possible. Model studies suggest that approximately 8% of the purified product is the diastereomer of βA4 containing D-Leu at position 17.[14,26] Epimerization can be reduced by running the final coupling at 4 °C.[14,26]

The synthetic product was cleaved from the resin and deprotected using HF.[27,28] The crude product contained three major components: βA4, β18–42, and β26–42. This mixture produced a broad, unresolved peak on RPHPLC, supporting the proposal that the C-terminus of βA4 determines its solubility[19] and demonstrating the difficulty of separating deletion impurities which would be produced in a stepwise synthesis.[14] However, the low molecular weight impurities from this fragment synthesis (β18–42 and β26–42) were completely removed by gel-filtration HPLC (Waters μ-styragel-HT) in hexafluoroisopropyl alcohol. The recovery of material from this column was quite high. The gel-purified material was then rechromatographed by RPHPLC to remove minor side products, including β1–37 (a small amount (ca. 5%) was present in the crude peptide) and benzylated βA4 which was, in some cases, produced during the deprotection step.[27,28] Purified synthetic βA4 (purity >90% by MS) was characterized by laser desorption MS and amino acid analysis. The sequence was confirmed by Edman degradation.[29]

Operationally, the synthesis of βA4 in our laboratory involves eight coupling reactions: four amino acid couplings followed by four fragment couplings. The overall chemical yield is 42% from the C-terminal resin-bound amino acid as compared to ca. 66% for an efficient (99% per coupling) stepwise synthesis. However, the material synthesized by the fragment coupling approach can be easily purified because it is devoid of deletion impurities. The economy of this convergent strategy makes it possible to produce multimilligram quantities of isotope-labeled analogs and sequence analogs of the βA4 protein for studies of the structure of AD amyloid plaque.

Acknowledgment. This research was supported by the Whitaker Health Sciences Foundation, the American Health Assistance Foundation (Alzheimer's Disease Research), the National Institute on Aging (AG08470-01), the National Science Foundation (Presidential Young Investigators Award), the Sloan Foundation, the Camille and Henry Dreyfus Foundation, Merck, Pfizer, Lilly, ICI, Monsanto, Hoechst-Celanese, Parke-Davis, and GE. P.L. is the Firmenich Career Development Assistant Professor of Chemistry. J.H. was a Whitaker Foundation graduate fellow, and K.H. was an NIH predoctoral trainee (1T32GM08318-01). We thank Dr. Ioannis Papayannopoulos of the MIT mass spectrometry facility (NIH Grant RR00317) and Ed Takach for mass spectral analysis and Richard Cook of the MIT Biopolymers Laboratory for sequencing and amino acid analysis.

(24) β(38–42)′-Ⓡ (Ⓡ = Merrifield resin, Figure 3) was synthesized by double couplings with acetylation after the second coupling. The peptide was cleaved[27,28] and analyzed by FABMS (β38–42 (calcd MW = 457.2) 458.2 (M + H)$^+$) and amino acid analysis (G 1.0 (1), V 2.1 (2), I 1.2 (1), A 1.0 (1)) to verify its composition and purity (>95%). β(26–42)′-Ⓡ was cleaved, deprotected, and sequenced by Edman degradation.

(25) Fragment coupling yields were determined by amino acid analysis and quantitative ninhydrin analysis of the resin-bound product.

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(29) Characterization of synthetic βA4: laser desorption MS (MW = 4514.1) 4515.0 (M + H)$^+$; amino acid analysis D/N 4.1 (4 calcd), E/Q 3.9 (4), S 1.9 (2), G 6.3 (6), H 2.4 (3), R 0.8 (1), A 3.9 (4), Y 0.8 (1), V 4.2 (6), M 1.1 (1), I 2.0 (3), L 2.0 (2), F 2.8 (3), K 1.8 (2). Edman degradation of the crude product confirmed the sequence through 36 cycles, with preview at the fragment junctions, as expected.

Simultaneous Coordination of a Ketone by Two Main-Group Lewis Acids†

Vijay Sharma, Michel Simard, and James D. Wuest*,[1]

Département de Chimie, Université de Montréal Montréal, Québec, H3C 3J7 Canada

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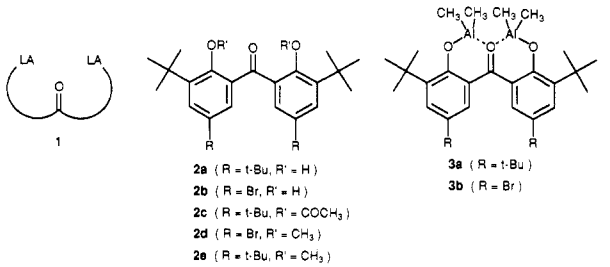
The carbonyl group of ketones and aldehydes is one of the most important functional groups in organic chemistry. Its intrinsically high reactivity can be enhanced by forming electrophilically activated complexes with Lewis acids.[2] In principle, simultaneous coordination by two or more Lewis acids could bring about multiple electrophilic activation, leading to even greater increases in reactivity and useful stereochemical effects.[3,4] However, it has not yet been established that ketones and aldehydes are basic enough to accommodate two main-group Lewis acids at the same time.[5,7] To test this possibility, we decided to synthesize a ketone **1** incorporating two nearby sites of Lewis acidity (LA). The carbonyl oxygen can interact with one site of Lewis acidity at a time, or it can interact symmetrically or unsymmetrically with both at once. We have found that simultaneous symmetric coordination is enthalpically feasible and that it has chemically significant consequences.



Suitable frameworks for juxtaposing a ketone and two sites of Lewis acidity were provided by 2,2′-dihydroxybenzophenones **2a**[8]

† Dedicated with affection and respect to Professor Frank H. Westheimer on the occasion of his 80th birthday.

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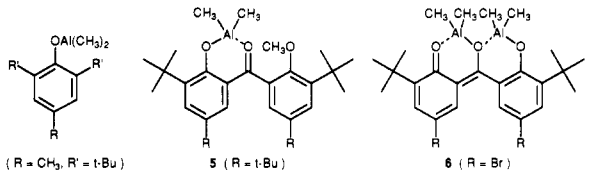
and **2b**.[9] Compound **2a** was prepared by the condensation of 2,4-di-*tert*-butylphenol with formaldehyde,[10] followed by acetylation (74%), oxidation to diacetate **2c** (CrO_3, Ac_2O, 33%),[11] and hydrolysis (79%).[12] In a similar way, compound **2b** was prepared from 4-bromo-2-*tert*-butylphenol[13] by condensation with formaldehyde (66%),[14] followed by methylation (CH_3I, KH, 80%), oxidation to diether **2d** (CrO_3, Ac_2O, 63%),[11] and demethylation (BBr_3, 80%).[12] Treatment with $Al_2(CH_3)_6$ then converted dihydroxybenzophenones **2a** and **2b** into aluminum phenoxides **3a** and **3b**, which were isolated as ruby-red crystals in 74% and 59% yields, respectively.[12,15,16]

Comparison of the carbonyl stretching frequencies of aluminum phenoxide **3a** (1540 cm^{-1}) and the analogous diether **2e** (1645 cm^{-1})[17a] shows that the carbon–oxygen double bond has been markedly weakened by coordination of at least one atom of aluminum. The ^{27}Al NMR spectrum of compound **3a** ($CDCl_3$, 25 °C) consists of a single broad peak at δ 142 ($\omega_{1/2}$ = 14 000 Hz), which is characteristic of tetracoordinate aluminum[18] and similar to the signal observed for the related benzophenone complex of aluminum phenoxide **4**.[19a,b] The low-temperature ^{13}C NMR



4 (R = CH_3, R' = t-Bu) 5 (R = t-Bu) 6 (R = Br)

spectrum of aluminum phenoxide **3a** (Figure 1) shows that the structure is symmetric in solution or that the carbonyl oxygen moves rapidly from one aluminum to the other.[20] Since benzophenones adopt characteristic C_2 conformations,[21] the nonequivalence of the two CH_3 groups on each aluminum is fully consistent with symmetric structure **3a**. Unexpectedly, the carbonyl carbon (δ 196.8) appears upfield of that of the analogous diether **2e** (δ 197.6), whereas the corresponding signal in the simple chelate **5**[17b] has a normal downfield shift (δ 202.6).[19a,c]

Definitive evidence that the carbonyl oxygen interacts simultaneously and symmetrically with both aluminums was provided by an X-ray crystallographic study of compound **3b**.[22] The C_2-symmetric structure is shown in Figure 2, along with selected interatomic distances and angles. Although the standard deviations in the structural parameters are too high to permit a detailed comparison with other compounds, the structure of aluminum phenoxide **3b** clearly incorporates unusual features that result from simultaneous coordination of the carbonyl oxygen by two Lewis acids. Specifically, the carbon–oxygen double bond (1.34 (2) Å) has been lengthened dramatically, making it comparable in length to the phenoxy O(1)–C(1) single bonds (1.32 (2) Å).[23] This means that resonance hybrid **6** must contribute to the structure despite a partial loss of aromaticity. The upfield shift of the carbonyl carbon, the short O(1)–C(1) distances, and the close similarity of the C(1)–C(6) and C(6)–C(7) distances support this conclusion. In addition, the phenoxy Al–O(1) distances (1.78 (1) Å) are longer than expected (1.73 (1) Å),[19a] presumably because resonance hybrid **6** contributes to the structure and because chelation reduces Al–O(1) π-bonding by forcing the C(1)–O(1)–Al angles to close to 122 (1)°.[24] The Al–O(2) dative bonds (1.96 (1) Å) are both longer than the corresponding distance in the benzophenone complex of aluminum phenoxide **4** (1.91 (1) Å).[19a] This is presumably because the carbonyl oxygen in compound **3b** is shared by two aluminums and because the strong preference for a C_2 conformation further weakens the Al–O(2) bonds by forcing the two Lewis acids out of the carbonyl plane,[2] creating Al–O(2)–C(7)–C(6) dihedral angles of 8.3 (1)°. Detailed examination of the geometry around aluminum provides additional evidence that the two Al–O(2) dative bonds are weakened. Specifically, the sum of the three angles at Al involving O(1), C(8), and C(9) is large (346 (1)°) and the O(1)–Al–O(2) angle is small (92 (1)°), indicating that the geometry around aluminum should be described as distorted trigonal rather than tetrahedral.[25] Even though the two dative bonds are weakened, however, symmetric structures **3a** and **3b** are nevertheless more stable than unsymmetric alternatives in which one aluminum is coordinated and the other is free.

For the following reasons, we believe that the symmetric doubly-coordinated structures are intrinsically favorable and not merely a consequence of special steric effects. Since the phenoxy C(1)–O(1)–Al angles are significantly more closed than those of related aluminum phenoxides and their complexes,[24] the enthalpic effect of double coordination must be large enough to compensate for reduced Al–O(1) π-bonding. In addition, ^{13}C NMR spectra (CD_2Cl_2, −85 °C) show that added benzophenone does not bind to the aluminums of phenoxide **3a**. Since sterically hindered analogue **4** forms a benzophenone adduct, this experiment provides an important measure of the strength of double coordination.

This work is significant because it suggests that the simultaneous coordination of ketones and aldehydes by two main-group Lewis acids may be enthalpically feasible in simpler systems as well[26]

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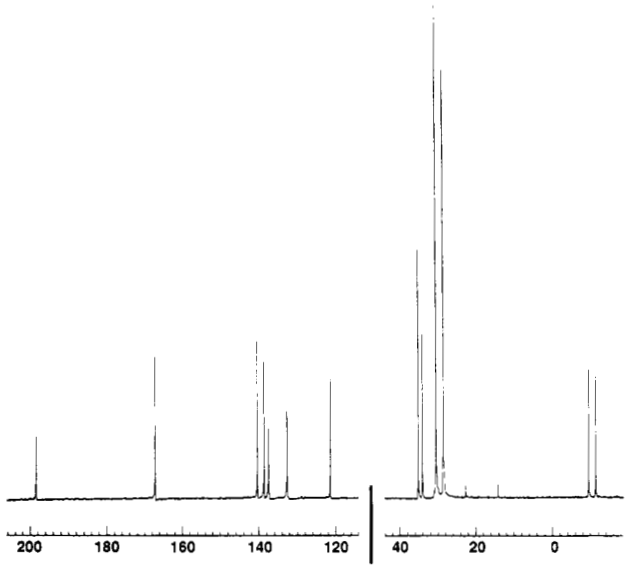

Figure 1. Proton-decoupled ^{13}C NMR spectrum of a 0.10 M solution of aluminum phenoxide **3a** in CD_2Cl_2 at −85 °C.

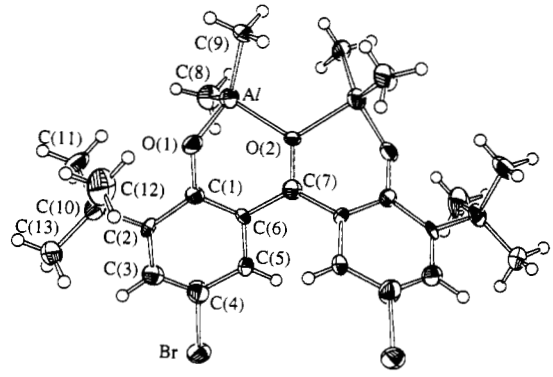

Figure 2. ORTEP drawing of the C_2-symmetric structure of aluminum phenoxide **3b**. Hydrogen atoms are shown as spheres of arbitrary size, and other atoms are represented by ellipsoids corresponding to 50% probability. Important interatomic distances (Å) and angles (deg) include O(2)–C(7) = 1.34 (2), Al–O(2) = 1.96 (1), Al–O(1) = 1.78 (1), O(1)–C(1) = 1.32 (2), C(1)–C(6) = 1.44 (3), C(6)–C(7) = 1.44 (2), O(1)–Al–O(2) = 92 (1), O(1)–Al–C(8) = 112 (1), O(1)–Al–C(9) = 110 (1), C(8)–Al–C(9) = 124 (1), and C(1)–O(1)–Al = 122 (1).

and may have useful chemical consequences, including enhanced reactivity of the carbonyl group.

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Supplementary Material Available: Spectroscopic and analytical data for compounds **3a** and **3b** and intermediates involved in their synthesis and description of the structure determination and tables of X-ray crystallographic data for compound **3b**, including atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and fixed hydrogen atom coordinates (10 pages); listing of observed and calculated structure factors for compound **3b** (6 pages). Ordering information is given on any current masthead page.

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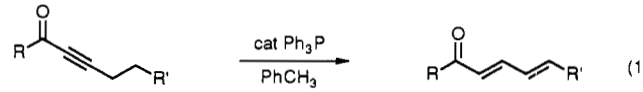
Internal Redox Catalyzed by Triphenylphosphine

Barry M. Trost* and Uli Kazmaier

Department of Chemistry, Stanford University
Stanford, California 94305-5080
Received April 20, 1992

Redox reactions constitute one of the fundamental types of transformations in a synthetic sequence. Adjustment of oxidation level by internal hydrogen reorganization is more atom economical than external sequential reduction–oxidation (or vice versa) processes. Such reactions have fallen almost exclusively into the domain of transition metal catalysts.[1-3] We wish to record a new type of catalysis by triphenylphosphine[4] that effects a remarkably facile isomerization of yne–carbonyl compounds to conjugated diene–carbonyl compounds,[5] which are common flavor constituents as well as important building blocks for complex targets.[6]

Warming a toluene solution of an ynone to 80–110 °C with 5–10 mol % of triphenylphosphine leads smoothly to the corresponding conjugated dienone (eq 1 and Table I). Both aromatic and aliphatic ketones successfully participate, but the latter require slightly higher temperatures (entry 1 vs 2 or 3).



(1)

Switching from a ketone to an ester as the acetylenic activating group allows the reaction to proceed but is best done in the presence of a weak acid such as acetic acid. The compatibility of both a benzyl ester (entry 4) and especially an allyl ester (entry 5), groups which may not survive transition metal catalyzed reactions, highlights the virtues of this unusual catalyst system. The less electron withdrawing amide (entry 6) requires somewhat

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(8) The facility of the R_3P-induced isomerization raises the question of its involvement in those isomerizations supposedly catalyzed by transition metal complexes containing such ligands; see ref 5.

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