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Notes

Iron-Promoted Deamination Reactions of N-Substituted 7-Azanorbornadiene Derivatives

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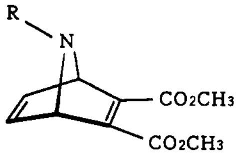
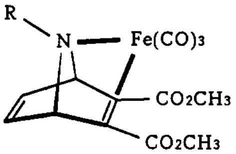
Summary: Two types of metallic intermediates were observed in the iron-promoted deamination reactions of N-substituted 7-azanorbornadiene (ANBD) derivatives, i.e., (ANBD)Fe(CO)$_4$ formed first, followed by (ANBD)-Fe(CO)$_3$. The latter can also be prepared alternatively from the former by reacting with trimethylamine N-oxide. Their spectroscopic characteristics as well as their roles in the deamination mechanisms were analyzed.

Introduction

Thermolysis of 7-substituted 7-azanorbornadiene (ANBD) derivatives of **1** with iron carbonyls is known to result in the formation of phthalate through nitrene-extrusion reactions. The intermediate iron carbonyl complexes, i.e., **2a-e** and **3a-d**, have been isolated.[2a] The structures of **2a** and **2d** were confirmed by X-ray crystallography, whereas other derivatives of **2** and **3** were assigned according to their NMR and IR spectroscopic features. In all the structures, the ANBD ligands were found to chelate the metal via their *exo* faces. From the crystal structure data for **2a** and **2d**, it was evident that a bond exists between the Fe and N atoms (Table I). The Fe–N bonding is considered to have played an essential role in the metal mediated nitrene-extrusion reactions.



1a) R = SO_2CH_3
b) R = $COCH_3$
c) R = $CO_2C_2H_5$
d) R = Ph
e) R = H
f) R = SO_2-p-$C_6H_4CH_3$



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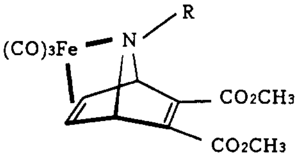

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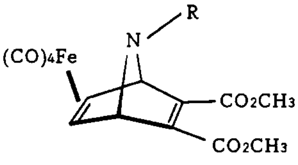

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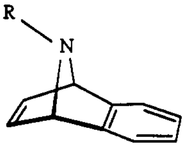
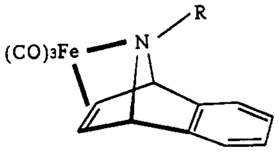
In our recent studies on analogous benzo-fused systems (**5**), we have found that, prior to the formation of (ANBD)-Fe(CO)$_3$ complexes (**6**), there exist stable (ANBD)Fe(CO)$_4$ (**7**) complexes.[3] The crystal structures of **7a**, **7g**, and **7h** have been solved, showing no direct bonding between the Fe and N atoms. This new finding has prompted us to reexamine our previous work on the complexes of **2** and **3**, and indeed, we have found that the structures of type **4** also exist in the reactions. In this report the roles of **4** and **7** in the nitrene elimination mechanism are investigated and the spectroscopic characteristics of **3** and **4** as well as those of **6** and **7** are compared.



5a) R = SO_2CH_3
c) R = $CO_2C_2H_5$
d) R = Ph
e) R = H
g) R = p-$C_6H_4CH_3$
h) R = p-C_6H_4Cl



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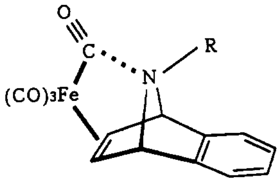

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Results and Discussion

Prior to the crystal structure analyses of **7a**, **7g**, and **7h**, the presence of (ANBD)Fe(CO)$_4$ in the mechanism of the nitrene-extrusion reaction was not recognized.[2] Although in these structures there is found no direct bonding

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(2) (a) Sun, C.-H.; Chow, T. J.; Liu, L.-K. *Organometallics* **1990,** *9,* 560. (b) Sun, C.-H.; Chow, J. J. *J. Chem. Soc., Chem. Commun.* **1988,** 535.

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Table I. Comparison of Atomic Distances (Å) among the Iron Carbonyl Complexes

	(ANBD)Fe(CO)$_3$		(ANBD)Fe(CO)$_4$		
	2a[a]	**2d**[a]	**7a**[b]	**7g**[b]	**7h**[b]
Fe—C(olefin)	2.000(3)	2.004(4)	2.075(4)	2.084(5)	2.084(5)
C═C	1.471(6)	1.456(6)	1.415(8)	1.423(7)	1.421(6)
Fe—N	2.059(4)	2.041(4)			
C—N			2.572(8)	2.261(6)	2.315(5)

[a] Reference 2a. [b] Reference 3.

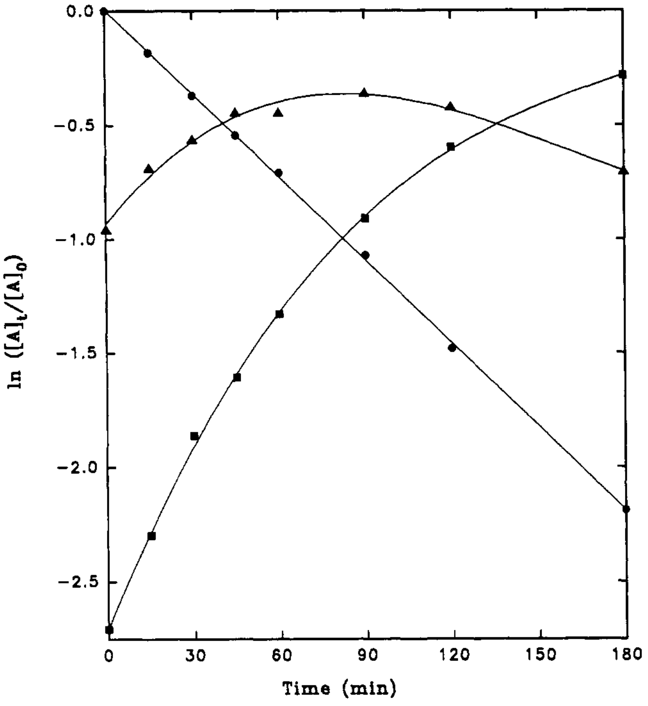

Figure 1. Kinetic measurements for the thermolyses of **6h** and **7h**. The plots of ln($[A]_t/[A]_0$) versus time are shown for **6h** (▲), **7h** (●), and naphthalene (■), where $[A]_t$ represents the concentration of the substrates and $[A]_0$ is the initial concentration of **7h**. The straight line corresponding to the disappearance of **7h** (●) indicates that it follows the first order rate law.

between the Fe and N atoms, an unusual nonbonded attractive force does exist between the coordinated CO groups and the nitrogen atoms. The distance between C(O) and N is measured to be in the range of 2.26–2.57 Å (Table I),[3] significantly shorter than the sums of the van der Waals radii. The Fe—C═O angle bends away from the N atom, forming an angle of 161–168°. This attractive interaction may have accelerated the process of CO elimination in the subsequent conversion of **7** to **6**. The force must be quite weak since, in solution at room temperature, the four CO groups exchange positions so rapidly that their absorptions in the ^{13}C NMR spectrum coalesce into one signal. Upon heating, one of the CO groups is eliminated to yield the corresponding structure of **6**. Continuous heating of **6** results in the extrusion of nitrene to yield naphthalene as the final product.

A simple kinetic experiment can be performed using NMR as a probe to monitor the reacting sequence. A mixture of **6h** and **7h** was dissolved in C_6D_6 containing an internal standard. The solution was then sealed in an NMR tube and heated in a thermostat maintained at 70 °C. The integrals of the proton signals were recorded and normalized, and the result is plotted in Figure 1. The disappearance of **7h** follows a first order rate law, as indicated by the linear relationship of ln(A_t/A_0) versus time, with an estimated rate constant of 2.03×10^{-4} s^{-1}. The concentration of **6h** increases during the first hour and then decreases after 2 h. Such a reaction sequence [**7h** → **6h** → naphthalene] is observed in all the complexes of types **7** as well as **4** in general.

In a similar treatment, the thermal decomposition rate of **6h** (using a purified sample) is measured to be 7.67×10^{-5} s^{-1}, which is about 2.65 times slower than that of **7h**. Since both processes proceed rather slowly at ambient conditions, such a rate difference allows us to collect both **6h** and **7h** in pure forms during the course of the reaction. However, this situation may not be applicable for the other systems, e.g. **2**–**4**.

In the reaction of **1** with iron carbonyl, both the *exo* faces of ANBD are capable of chelation to form the complexes of types **2** and **3**. Previous information indicates that the complexes of type **2** are somewhat more stable than those of type **3**.[4] For type **2** complexes, only the tricarbonyl form of (ANBD)Fe(CO)$_3$ is observed, whereas for type **3** both forms of (ANBD)Fe(CO)$_3$ (**3**) and (ANBD)Fe(CO)$_4$ (**4**) are detectable in the reaction. In nearly all the experiments, the isolated yields of **2** are higher than those of **3** and **4** combined. In the sequence **4** → **3** → phthalate, the second step proceeds much faster than the first step, so that it is unlikely to collect **3** directly upon heating. To obtain **3** in pure form, an alternate procedure must be employed in order to liberate 1 mol of CO from **4**.

Transformation of (ANBD)Fe(CO)$_4$ (both **4** and **7**) to (ANBD)Fe(CO)$_3$ (**3** and **6**) can be achieved smoothly at room temperature by reacting them with trimethylamine *N*-oxide. In a control experiment, the process **4a** → **3a** was monitored by UV absorption spectrophotometry. To a quartz cell containing **4a** in methanol was added an excess amount of anhydrous trimethylamine *N*-oxide. The cell was scanned by the spectrophotometer at 10-min intervals at ambient temperature until nearly all the **4a** was consumed, which happened in about 1 h. The result showed (Figure 2) that the λ_{max} of **4a** occurring at 305 nm diminished to a shoulder while the absorbance of **3a** in the region around 400 nm increased. Prolonged standing of the cell resulted in an immediate further decomposition of **3a**.

The spectroscopic difference between the structures of (ANBD)Fe(CO)$_4$ and (ANBD)Fe(CO)$_3$ are not apparent but can be distinguished by careful analysis. Their molecular ions in the mass spectra are rather difficult to observe due to their unstable nature. The metal-coordinated olefin moieties show different upfield shifts in the ^{1}H and the ^{13}C NMR, versus the free olefins. In the ^{13}C NMR, the signals of (ANBD)Fe(CO)$_3$ (δ 43–49) are shifted more upfield than those of (ANBD)Fe(CO)$_4$ (δ 58–61), whereas in ^{1}H NMR the relative amounts of shift are of the opposite order (δ 4.1 vs 3.5). In Tables II and III, the chemical shifts for the pairs of compounds **3**/**4** and **6**/**7** are listed for a comparison. In the IR, the highest CO stretching frequencies can also be used as a criterion to differentiate the two complexes. The absorption frequencies for (ANBD)Fe(CO)$_4$ show a hypsochromic shift of ~30–40 cm^{-1} compared to those of (ANBD)Fe(CO)$_3$ (Table IV). The shifting of frequencies can be ascribed to a stronger electron-withdrawing ability of the CO ligand

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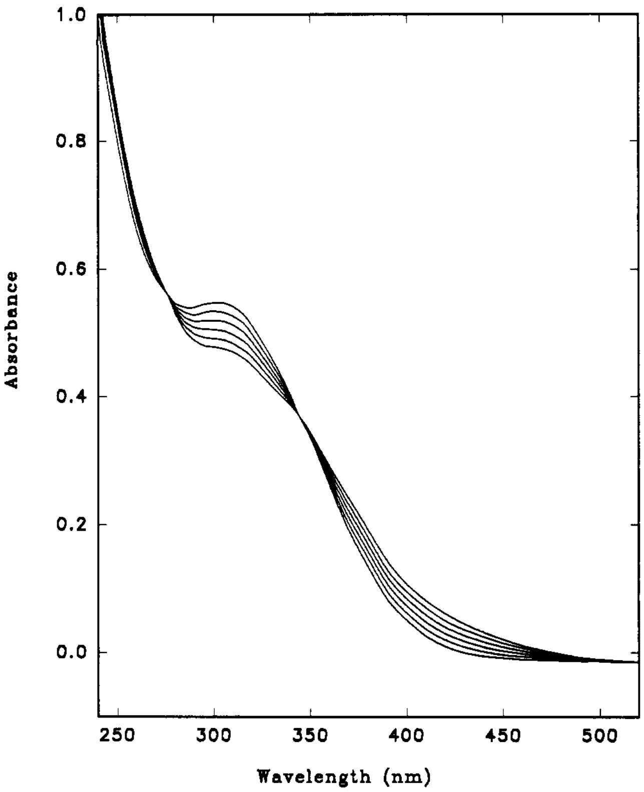

Figure 2. UV absorption spectra taken in 10-min intervals for the reaction of **4a** with trimethylamine *N*-oxide. The initial λ_{max} at 305 nm of **4a** diminishes as it is gradually converted to **3a**. The reaction is virtually complete in 1 h.

Table II. ^{13}C NMR Chemical Shifts for the Metal-Coordinated Olefin Protons in Complexes 3, 4, 6, and 7 (δ Unit from TMS in $CDCl_3$)

(ANBD)Fe(CO)$_3$		(ANBD)Fe(CO)$_4$	
3a	42.7	**4a**[a]	57.6
3f	43.0	**4f**	58.1
6g	48.9	**7g**[b]	61.2
6h	49.0	**7h**[b]	61.1

[a] Reference 2a. [b] Reference 3.

Table III. ^1H NMR Chemical Shifts for the Olefin Protons in Complexes 3, 4, 6, and 7 (δ Unit from TMS in $CDCl_3$)

(ANBD)Fe(CO)$_3$		(ANBD)Fe(CO)$_4$	
3a	4.11	**4a**[a]	3.50
3c	4.14	**4c**[a]	3.55
3f	4.02	**4f**	3.42
6d	4.15	**7a**[b]	3.35
6e[a]	4.01	**7c**[a]	3.55
6g	4.14	**7g**[b]	3.51
6h	4.16	**7h**[b]	3.52

[a] Reference 2a. [b] Reference 3.

relative to the amino group, which results in the reduction of total electron density around the metal and consequently reduces the amount of back-donation from the metal to each CO. The metal–olefin coordination in **4** is expected to be weaker than those in **2** and **3**. From Table I it is evident that the bonding distances between the metal and the olefin carbons in **2a** and **2d** are significantly shorter than those in **7a**, **7g**, and **7h**, whereas the order of bond lengths of C=C is just the opposite.

With such an awareness, our previous assignments[2a] for structures **3a**, **3c**, and **6c** need to be reassigned to structures of **4a**, **4c**, and **7c**, respectively. The empirical formula of **4a** is reconfirmed by its elemental analysis,[5] and **3a** is prepared now from **4a**, as mentioned earlier. The analogous *N*-tosyl derivative (**1f**) has also been prepared, and in its reaction with iron carbonyl the two complexes **2f** and **4f** are isolated in 48% and 25% yields, respectively. Complex **3f** is produced in pure form from **4f** upon treatment with trimethylamine *N*-oxide. The reaction sequence **1** → **4** → **3** → phthalate is clearly demonstrated in this example.

Table IV. CO Stretching Frequencies (ν, cm^{-1}) for Complexes 3, 4, 6, and 7 (KBr Otherwise Indicated)

(ANBD)Fe(CO)$_3$		(ANBD)Fe(CO)$_4$	
3a[c]	2051, 1975	**4a**[a]	2095, 2015, 1985
3c[c]	2045, 1965	**4c**[a]	2095, 2000, 1985
3f[c]	2049, 1965	**4f**	2087, 2015, 1975
6d	2018, 1946, 1922	**7d**	2067, 2004, 1965, 1942
6g	2016, 1947, 1927	**7g**[b]	2068, 2000, 1965
6h	2024, 1946, 1932	**7h**[b]	2074, 2010, 1976, 1949

[a] Reference 2a. [b] Corrected values from ref 3. [c] In CH_2Cl_2.

The nitrene moiety extruded from the ANBs is in a metal-coordinated form, which, upon hydrolysis, produces the corresponding amines. For **1a** and **1f**, for example, the yields of sulfonamides are quite high (ca. 90%).[2a] The yields of anilines in the fragmentations of **6d**, **6g**, and **6h** are variable depending on the nature of the phenyl substituents. In addition to amines, other side products also appear in the reactions. In the thermolysis of **6d** for example, it is interesting to identify the presence of diphenylurea (25%) in the reaction mixture along with aniline (13%). The carbonyl group in diphenylurea (PhNH–CO–NHPh) must be derived from the iron carbonyl ligands. The detailed structure of the nitrene–iron complex immediately after the fragmentation is not quite clear at present due to its transient existence.

Conclusion

Thermolysis of N-substituted ANBD derivatives with iron carbonyl results in the extrusion of the nitrene moieties. For the derivatives of 2,3-dicarbomethoxy-ANBD (**1**), the intermediate compounds of type **3** are not readily detectable since the rates of their formation (from **4**) are much slower than the rates of their decomposition (to form the phthalate). For the benzo-fused ANBD derivatives (**5**), the corresponding rates are of the opposite order so that both compounds **6** and **7** could be isolated during the course of the reactions. Compounds of types **3** and **6** can be prepared alternatively from either **4** or **7** upon treatment with trimethylamine *N*-oxide. All these compounds were found to act as the reactive intermediates in the nitrene-extrusion reactions.

Experimental Section

^1H and ^{13}C NMR spectra were obtained on either a Brucker AMX-500 or an AC-200 FT spectrometer. Infrared spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. Elemental analyses were obtained on a Perkin-Elmer 2400 EA instrument. Mass spectra were carried out on a VG Analytical 70-250 S/SE spectrometer. Melting points were measured by a Yanato MICRO mp apparatus model MP-S3 and were uncorrected.

(2,3-Dicarbomethoxy-7-(*p*-tolylsulfonyl)-7-azanorbornadiene)tricarbonyliron (2f) and the Corresponding Tetra-

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(5) Anal. Calc for $C_{15}H_{13}FeNSO_{10}$ (**4a**): C, 39.58; H, 2.88; N, 3.08. Found: C, 39.42; H, 2.54; N, 3.02.

carbonyliron Complex 4f. To a round-bottom flask fitted with a nitrogen gas inlet was added under nitrogen atmosphere 7-azanorbornadiene (460 mg, 1.27 mmol), diiron nonacarbonyl (560 mg, 1.54 mmol), and degassed THF (120 mL). The solution was stirred at room temperature for 20 h. The resulting mixture was filtered, and the filtrate was concentrated *in vacuo*. The yellow residue was purified by passing it through a silica gel chromatographic column eluted with *n*-hexane/ethyl acetate (2/1 v/v). Complex **2f** (330 mg, 48%) was recrystallized from *n*-hexane/ethyl acetate, mp 100.5–102 °C dec. ^{1}H NMR ($CDCl_3$): δ 2.44 (s, 3H), 3.75 (s, 6H), 5.39 (t, J = 1.3 Hz, 2H), 6.01 (t, J = 1.3 Hz, 2H), 7.30 (d, J = 8 Hz, 2H), 7.47 (d, J = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.76, 51.92, 55.05, 82.26, 129.28, 130.42, 132.04, 138.80, 146.42, 172.70, 207.56. IR (KBr): ν 2063, 1992, 1972 cm^{-1}. Anal. Calcd for $C_{20}H_{17}FeNSO_9$: C, 47.73; H, 3.40; N, 2.78. Found: C, 47.56; H, 3.36; N, 2.68. Complex **4f** (170 mg, 25%) was recrystallized from ethyl acetate, mp 89–92 °C dec. ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 3H), 3.42 (s, 2H), 3.68 (s, 6H), 4.95 (s, 2H), 7.24 (d, J = 8 Hz, 2H), 7.47 (d, J = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.47, 51.97, 58.11, 69.98, 128.38, 129.97, 134.23, 144.37, 144.70, 162.56, 207.29. IR (KBr): ν 2087, 2015, 1975 cm^{-1}. Anal. Calcd for $C_{21}H_{17}FeNSO_{10}$: C, 47.36; H, 3.28; N, 2.79. Found: C, 47.48; H, 3.23; N, 2.64.

General Procedure for the Reaction of Tetracarbonyliron Complexes with Trimethylamine *N*-Oxide. Anhydrous trimethylamine *N*-oxide was prepared according to the literature.[6] To a stirring solution of the tetracarbonyliron complexes (i.e. 4 or 7, ca. 0.01 mmol) in acetone (10 mL) was added trimethylamine *N*-oxide (ca. 0.02 mmol). The mixture was stirred at room temperature for 2 min; it was then filtered and dried *in vacuo*. The yields of **3a** and **3f** were nearly quantitative. The products are not stable at room temperature and decompose readily while dissolved in solutions.

(2,3-Dicarbomethoxy-7-(methylsulfonyl)-7-azanorbornadiene)tricarbonyliron (3a). ^{1}H NMR ($CDCl_3$): δ 2.68 (s, 3H), 3.92 (s, 6H), 4.11 (s, 2H), 5.56 (s, 2H). ^{13}C NMR ($CDCl_3$, −40 °C): δ 39.6, 42.7, 53.2, 81.3, 144.6, 161.5, 209.4, 211.7. IR (CH_2Cl_2): ν 2051, 1975 cm^{-1}.

(2,3-Dicarbomethoxy-7-(*p*-tolylsulfonyl)-7-azanorbornadiene)tricarbonyliron (3f). ^{1}H NMR ($CDCl_3$): δ 2.44 (s, 3H), 3.72 (s, 6H), 4.02 (s, 2H), 5.56 (s, 2H), 7.30 (d, J = 8 Hz, 2H), 7.53 (d, J = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, −40 °C): δ 21.8, 43.0, 52.6, 82.0, 128.7, 130.0, 130.3, 143.3, 147.2, 160.9, 209.9, 211.9. IR (CH_2Cl_2): ν 2049, 1965 cm^{-1}.

(7-(*p*-Chlorophenyl)-7-azabenzonorbornadiene)tricarbonyliron (6h). Mp: 130–131 °C dec. ^{1}H NMR ($CDCl_3$): δ 4.16 (s, 2H), 5.38 (s, 2H), 5.68 (s, 2H), 6.72–7.26 (m, 8H, phenyl). ^{13}C NMR ($CDCl_3$): δ 48.89, 84.55, 119.14, 122.05, 127.31, 129.22, 131.16, 142.53, 146.82, 213.31. IR (KBr): ν 2024, 1946, 1932 cm^{-1}.

NMR Kinetic Measurement for the Thermolyses of 6h and 7h. A 5-mm-o.d. NMR tube containing C_6D_6 was filled with a mixture of the metal complex **6h** and **7h** (10 mg combined) and heptacyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]tetradecane[7] as an internal standard (singlet at δ 1.83). The tube was sealed and immersed in a thermostat maintained at 70 °C (±0.5 °C). The disappearance of metal complex was monitored by its ^{1}H NMR signal integrations. The tube was periodically withdrawn from the oil bath and subjected to spectroscopic measurements after cooling and filtration. The signals used for kinetic measurements are those of the olefin hydrogens (δ 3.0 for **7h**, 3.82 for **6h**)[8] and the bridgehead hydrogens (δ 4.02 for **7h**, 5.03 for **6h**) of the metal complexes and the signal at δ 7.60 for naphthalene. In these regions the absorption peaks are generally well separated. The measurements were completed at ca. 80% consumption of the starting materials.

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[8] The signals are all upfield-shifted in C_6D_6 compared to those measured in $CDCl_3$, as shown in Table III.