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(METHYLENECYCLOPROPANE)IRON TETRACARBONYL COMPLEXES: OPTICAL ACTIVITY, EPIMERIZATION, AND CARBON-13 NMR SPECTRA

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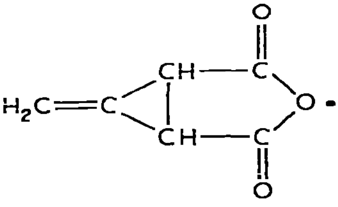
Summary

The synthesis of (diethyl 1-methylene-*trans*-2,3-cyclopropanedicarboxylate)iron tetracarbonyl in optically active form is described. This complex was oxidized with cupric bromide, and yielded its original *trans*-Feist's ester precursor with full retention of optical activity. The iron tetracarbonyl complex of the *cis* isomer was epimerized to the *trans* complex by sodium ethoxide in ethanol. A description of the nature of the bonding between the olefin and the metal in these complexes was derived from carbon-13 magnetic resonance experiments.

Introduction

The first successful synthesis of an intact (methylenecyclopropane)iron tetracarbonyl complex (II) from the anhydride I, was described in 1973 [1], and followed repeated reports of ring opening reactions leading to (trimethylenemethane)iron tricarbonyl complexes instead. The surprising disclosure by Krull [2] that he had obtained the iron tricarbonyl complexes of *cis* and *trans* Feist's dimethyl ester (V and VI from IIIb and IVb, respectively) therefore contrasted with the same author's synthesis of II [1]. However, the structures were recently corrected to VIIb and VIIIb respectively, on the basis of chemical [3] and crystallographic data [4].



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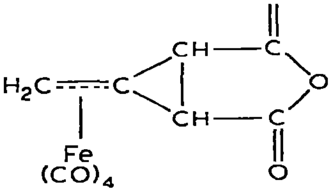

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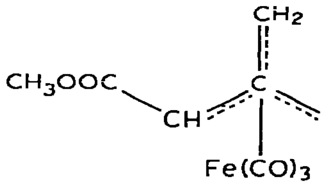

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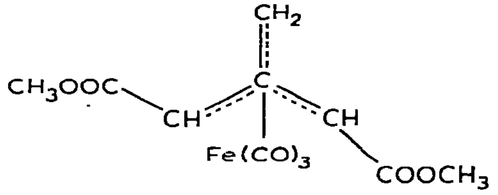

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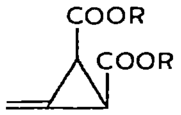

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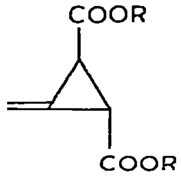

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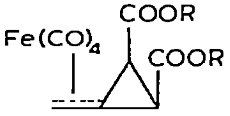

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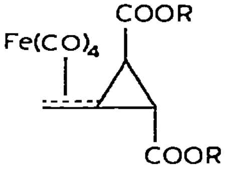


(VIII)

(a, R = C_2H_5; b, R = CH_3)

We had been engaged in similar studies, and wish to describe the isolation of the first optically active (methylenecyclopropane)iron tetracarbonyl complex, its oxidation to the original methylenecyclopropane precursor with full retention of optical activity, as well as the first example of base-catalyzed epimerization of a substituted (methylenecyclopropane)iron tetracarbonyl complex (Scheme 1). The first carbon-13 magnetic resonance (CMR) data of such complexes are also presented, providing a picture of the metal to olefin bonding involved.

Results and discussion

The reaction of the Feist's diethyl esters IIIa and IVa with diiron nonacarbonyl in benzene at room temperature was followed by PMR. It proceeded to completion, yielding VIIa and VIIIa, respectively. Their purification by crystallization could not be achieved, but pure samples were obtained following extraction by hexane and column chromatography. The tetracarbonyl structural assignments were deduced from the mass spectra which showed the molecular ion at *m/e* 366, the elemental analysis, as well as from the results of oxidation reactions.

The much slower rate of formation for the complexes of the ethyl esters compared to the methyl esters was best explained by a steric rather than electronic effect, and required the iron carbonyl moiety in VII to be *cis* to the ester groups, as confirmed by X-rays [4].

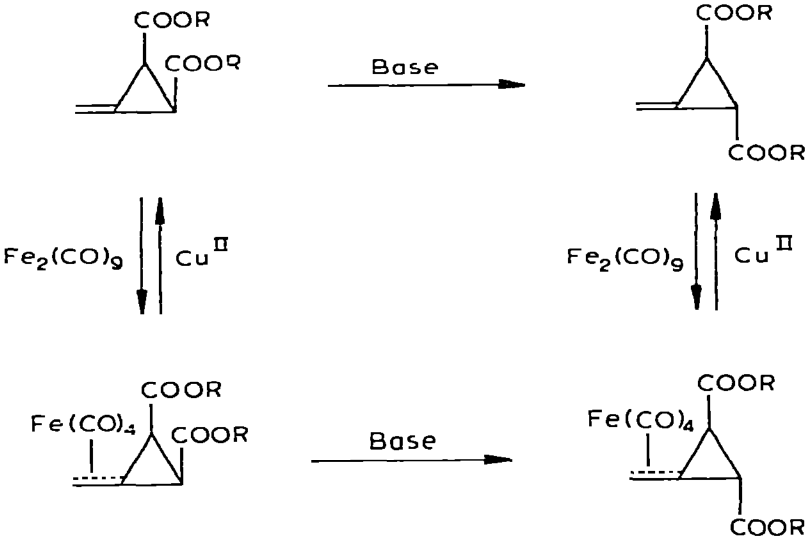
The oxidation of VII to III had not been reported by previous workers [2,3]. We found that each complex yielded its parent Feist's ester when treated with cupric bromide, although in the case of VIIa a brominated product was also formed in small yield in one experiment. This product is believed to be diethyl *trans*-3-bromo-*cis*-3-bromomethyl-*cis*-1,2-cyclopropanedicarboxylate (IX), based on both the mass spectrum which showed the molecular ion at *m/e* 356 with the characteristic isotopic distribution of a dibrominated substance, and the PMR spectrum in benzene which displayed a triplet at 1.05 and a quartet at 4.10 for the two esters, as well as two sharp singlets of equal intensity at 2.03 (CH_2Br) and 3.17 ppm (two ring protons). The stereochemistry follows from mechanistic considerations, where the electrophilic attack by the bromine would proceed from the less hindered side of either IIIa or VIIa. The less likely possibilities that either the *trans* addition of bromine had proceeded from the more hindered side, or that *cis* addition had taken place have not been rigorously excluded. Although the reaction was not scrutinized, we found that, as expected, the above product was also formed by treatment of IIIa with cupric bromide in benzene.

When the oxidation of VIIa was performed with ceric ammonium nitrate, the reaction was very clean, and IIIa was the only product which was detected.

The treatment of the *cis*-complex VIIa with sodium ethoxide in ethanol under nitrogen for 5 minutes at room temperature converted it into its *trans* isomer VIIIa irreversibly, and the similarly facile epimerization of the parent ester IIIa into IVa was also known [5] (Scheme 1).

SCHEME 1.

The interconversion of the Feist's esters and their iron tetracarbonyl complexes.



The resolution of Feist's acid was performed according to Doering and Roth [6], and the (+)-acid was treated with diazoethane in ether to yield the diethyl ester (+)-IVa, m.p. 50°, $[\alpha]_{320}^{20}$ 380° (*c* 0.2 in ethanol). The reaction of this ester with diiron nonacarbonyl, in turn, yielded (—)-VIIIa with $[\alpha]_{320}^{20}$ 840° (*c* 0.12 in ethanol). Finally, the oxidation of (—)-VIIIa with cupric bromide in benzene yielded back (+)-IVa which, after recrystallization, had its full optical activity with $[\alpha]_{320}^{20}$ 400° (*c* 0.19 in ethanol).

The above data, which were obtained before Whitesides's recent publications, contradicted Krull's conclusions [2] and clearly supported the fact that the integrity of the methylenecyclopropane system had not been disrupted during the process of forming the iron carbonyl complexes of the Feist's esters. The

TABLE 1

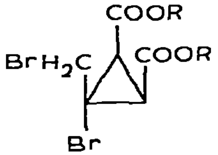
CMR DATA

The chemical shifts are in ppm from TMS, the C,H coupling constants in Hz are in parentheses.

Compound	Solvent	C(1)	C(2)	C(3)	CH_2	CO	OCH_2	CH_3	$Fe(CO)_n$
IIIb	CCl_4	25 (178)	*a*	128	108 (164)	168		53 (147)	
IVb	CCl_4	26 (165)	*a*	130	107 (165)	169		53 (147)	
VIIb	C_6D_6	29 (168)	*a*	50	23 (160)	170		51 (147)	209
VIIIb	C_6D_6	30 (169)	33 (172)	55	24 (162)	170 172		52 (147)	208
IIIa	C_6D_6	25	*a*	128[b]	107	167	61	14	
IVa	C_6D_6	26	*a*	128[b]	106	169	61	14	
VIIa	C_6D_6	29	*a*	50	23	169	61	14	209
VIIIa	C_6D_6	31	33	55	24	168 170	61	14	208
i	$CDCl_3$	26 (194)	*a*	124	108 (167)	165			
ii	$(CD_3)_2SO$	31 (187)	*a*	56	19 (162)	168			207
		33 (187)		57	23 (165)	169			208
X[c]	$CDCl_3$[7]	3	*a*	131	103				
XI[c]	CS_2[8]	53	*a*	105	53				212
XII[d]	neat			129 (167)	130 (162)	166		51 (147)	
XIII[d]	CS_2			44 (162)	34 (163)	174		51 (146)	208

[a] Equivalent to C(1). [b] Overlapping the solvent signal. [c] A numbering system similar to that of the Feist's esters is used for convenience. [d] For ease of comparison, C(1) and C(2) are aligned with the corresponding double bond carbons of the methylenecyclopropane derivatives.

CMR data on these compounds further reinforced the picture. The relative simplicity of the structures made it possible to utilize the undecoupled spectra in addition to the decoupled spectra, and the chemical shift assignments were therefore unambiguous (Table 1).



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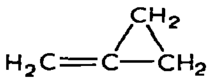
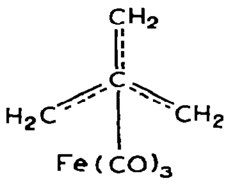


(X)



(XI)

The CMR data on the couple methylenecyclopropane X—(trimethylenemethane)iron tricarbonyl (XI) have been reported [7,8], and a comparison with the Feist's esters and their iron carbonyl complexes is informative. The 3-carbon in VIIb and VIIIb is shifted by 78 and 75 ppm upfield from the values in IIIb and IVb, respectively, about three times as much as the corresponding shift of 26 ppm in the parent hydrocarbon system. Similarly, the methylene carbon experienced a shift of 85 and 83 ppm going from IIIb and IVb to VIIb and VIIIb, respectively, compared to only 50 ppm for the hydrocarbon. It is therefore clear that both carbon atoms of the original double bond in the Feist's esters acquired a considerable amount of sp^3 character when converted into their iron carbonyl complexes, in sharp contrast with the parent system where the central carbon at 105 ppm remained in the range of typically sp^2 bonded carbons*.

It would have been informative to compare the shifts observed in this study with those experienced by simple methylenecyclopropanes or 1,1-dialkyl-substituded olefins upon iron tetracarbonyl complex formation. Unfortunately, these complexes are too unstable to be isolated. In their absence, the range of the CMR study was broadened by including the spectra for methyl acrylate (XII) and its stable iron tetracarbonyl complex XIII [10]. The shifts experienced by the olefin carbons upon complexation were 85 and 96 ppm, in reasonable agreement with the values observed in the methylenecyclopropane derivatives (Table 1).

The large upfield shifts observed for the methylene and C(3) carbons in the (methylenecyclopropane)iron tetracarbonyl complexes can be understood in terms of either the qualitative Dewar—Chatt—Ducanson model [11-13], or the Buckingham—Stephens model [14,15]. In the first model one postulates that the bonding with the metal involves a σ-coordinate bond between the highest filled π-bonding olefin orbitals and metal orbitals of σ-rotational symmetry, as well as a "back-bond" between the lowest lying antibonding π^*-orbitals of the olefin and filled orbitals of suitable symmetry on the metal. The observed upfield shifts, which correspond to increased shielding (i.e. greater electron density on the carbon, or increased sp^3 character), strongly suggest that bonding occurs by back-bonding from the metal to the π^*-olefin orbitals.

In the second model the upfield shifts observed in the iron tetracarbonyl complexes are attributed mainly to paramagnetic shielding of the carbons by the partially filled metal *d*-orbitals. Within the framework of this model, the greater upfield shift observed for the methylene carbon relative to C(3) indicates that the methylene—iron bond is shorter than the C(3)—iron bond.

In solution, enhanced internal degrees of freedom (i.e. vibrations and substituent group rotations), in conjunction with solvation, will influence the metal—ligand bonds, but not necessarily to the same extent. The greater shift observed for the methylene than for C(3) suggests a tighter bonding of the metal to the methylene, in agreement with obvious steric constraints placed by the *cis* ester group or groups. The bonding picture derived from the CMR in solution is thus the opposite from that in the solid state where a tighter bonding of the metal to C(3) was observed [4], but where intermolecular lattice interactions must play a determining role.

As anticipated, the two saturated ring carbons C(1) and C(2), as well as the ester carbonyls, were non-equivalent in the CMR of the *trans* complexes. The comparison of the chemical shift and coupling constant for C(1) in the *cis* complex VIIb (29 ppm, *J*(C,H) 168 Hz) with the values in the *trans* isomer VIIIb leads to the assignment of the signal at 31 ppm (*J*(C,H) 169 Hz) to C(1), and that at 33 ppm (*J*(C,H) 172 Hz) to C(2) in the latter. Similarly, the ester carbonyl at 170 ppm is assigned to the group at C(1) in VIIIb.

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* For a recent review on the CMR of metal carbonyl compounds see ref. 9.

The CMR data are listed in Table 1, and include the ethyl esters and the anhydride, as well as their iron tetracarbonyl complexes (in the case of II, the mixture of isomers was not separated).

The PMR data on VII and VIII were also determined, and the assignments verified by deuterium labeling. All the PMR and CMR data indicated the formation of only one isomer for VII unlike the case of the anhydride. One remaining problem concerned the assignment of the methylene and methine proton signals in the complexes, since conflicting proposals had been made by Krull [2] and by Whitesides and Slaven [3]. We exchanged these methine protons for deuterium in IVa by treatment with sodium ethoxide in deuterated ethanol C_2H_5OD*, and the signal at 2.71 disappeared from the spectrum of the complex derived from this material. By analogy, the signal at 2.51 ppm was assigned to the methine protons in the *cis* complex.

The accidental equivalence of the chemically non-equivalent methine protons in VIII is surprising since the ester groups attached to these same carbon atoms displayed the anticipated magnetic non-equivalence, and this had originally led Whitesides and Slaven [3] to an erroneous interpretation of the spectra. When interpretated in the light of the later chemical and physical results, the shift reagent experiments reported by Krull [2] are in agreement with our assignments. However, his assignments for the anhydride complexes [1] must be revised, the signals at higher field belonging to the methylene rather than methine protons.

Experimental

The PMR spectra were measured on Varian A60-A or T-60 spectrometers and are reported on the δ-scale in ppm downfield from internal TMS, the ORD on a Durrum—Jasco SS-20 spectrometer, the mass spectra on AEI MS-30 or Perkin—Elmer 270 spectrometers, and the infrared spectra on a Perkin—Elmer 521 spectrometer. The melting points were determined on a micro hot stage and not corrected. The elemental analyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

NMR spectra

The PMR spectra were recorded on Varian T-60 or A-60A spectrometers except where indicated. The natural abundance CMR spectra were obtained at 22.63 MHz on a Bruker HFX-90 spectrometer operating in the pulsed Fourier transform (FT) mode. A Bruker B-KR 322s pulsed NMR spectrometer provided gated RF power amplification, and a NIC-293 controller served as a pulse programmer. Free-induction decays (FID) of 8K data points were accumulated on a Nicolet 1080 data system; typically 1K to 4K such transients were collected per sample. Proton noise decoupled CMR spectra were recorded first to obtain simplified spectra with full Overhauser enhancement. Undecoupled spectra of selected samples were then obtained using a gated-decoupling technique in which the FID following each pulse was collected during the first 1.0 sec of the total

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* The deuterium exchange in Feist's acids was described by Ettlinger and Kennedy [16a] and by Bottini et al. [16b, 16c].

5.2 sec delay time between pulses; in order to increase the S/N ratio through the Overhauser effect, the decoupler was switched on during the remainder of the delay time between pulses. Exponential weighting of the FID data prior to transformation provided further improvement of the apparent sensitivity. A ^{19}F internal field/frequency lock system was used; the lock substance was either hexafluorobenzene or a trichlorofluoromethane—TMS mixture contained in a 10 mm coaxial sample tube. The chemical shifts are referred to internal TMS, which was present either in benzene-d_6 solvent or in the lock substance. The transformed, phase-corrected real spectra provided chemical shift accuracy of 1.5 Hz per channel.

Synthesis of the iron carbonyl complexes

The syntheses of the methyl esters and the anhydride complexes were performed essentially as reported elsewhere and need not be repeated here. Benzene was used as solvent and the reactions were clean, and faster than previously reported. The complexes decomposed slowly upon standing at room temperature (the ethyl esters faster than the methyl esters), and were stored in a freezer. They were purified before use by dissolving them in hexanes, filtering the solution, and removing the solvent under vacuum. A typical experiment is described below.

(Diethyl 1-methylenecyclopropane-trans-2,3-dicarboxylate)iron tetracarbonyl (VIIIa)

A mixture of IVa (1.03 g, 5.21 mmol) and $Fe_2(CO)_9$ (2.06 g, 5.65 mmol) in 50 ml benzene was stirred at 38° under nitrogen for 13 h. The solvent and $Fe(CO)_5$ were removed under vacuum, hexane was added, and the brown precipitate filtered and washed with solvent. The green filtrate and washings were combined and concentrated under vacuum, and the residue chromatographed over silica gel. Benzene eluted 1.22 g of VIIIa (63.9% yield), which crystallized upon standing for 3 months in the cold, m.p. 22-22.5°; PMR ($CDCl_3$) 1.16 (t, 7 Hz, 3H), 1.18 (t, 7 Hz, 3H), 2.12 (d, 3 Hz, 1H), 2.26 (d, 3 Hz, 1H), 2.71 (s, 2H), 4.10 (q, 7 Hz, 2H), and 4.15 ppm (q, 7 Hz, 2H); IR (neat) 2115s, 2080w, 2029vs, 1996vs for the iron carbonyls, 1725s for the ester carbonyls, 2990w, 2915w, 2880w, 1475vw, 1465w, 1445w, 1390w, 1367m, 1325m, 1305s, 1257m(br), 1175s, 1160s, 1092w, 1075w, 1033m, 963w(br), 913w, 896w, 856w, 824w, 622s and 588s cm^{-1}.

Anal. found: C, 46.34; H, 4.01; O, 34.96. $C_{14}H_{14}O_8Fe$ calcd.: C, 45.93; H, 3.85; O, 34,96%.

(Diethyl 1-methylenecyclopropane-cis-2,3-dicarboxylate)iron tetracarbonyl (VIIa)

The procedure described above yielded VIIa as a brown oil, PMR ($CDCl_3$) 1.19 (t, 7 Hz, 6H), 2.05 (t, 1 Hz, 2H), 2.51 (t, 1 Hz, 2H) and 4.14 ppm (q, 7 Hz, 4H); IR (neat) 2130s, 2095w, 2040vs and 1997vs for the iron carbonyls, 1737 for the ester carbonyls, and 3005m, 2960w, 2928w, 2892w, 1500w, 1475w, 1464w, 1445w, 1430w, 1390w, 1370m, 1337m, 1291m, 1263w, 1198s, 1177s, 1167s, 1100m, 1020m, 918w, 897w, 870w, 848w, 830w, 782w, 630s and 593s cm^{-1}. Anal. found: C, 46.31; H, 3.98; O, 34.29. $C_{14}H_{14}O_8Fe$ calcd.: C, 45.93; H, 3.85; O, 34.96%.

Epimerization of VIIa

The complex VIIa (0.427 g, 1.17 mmol) was added to a solution of sodium ethoxide (1.61 g, 23.7 mmol) in 25 ml of ethanol, and kept under N_2 for 30 min. After neutralization with glacial acetic acid, concentration under vacuum, extraction with hexanes, and concentration of this extract, the NMR of this product was that of almost pure VIIIa. When a pure sample of VIIIa was treated in the same conditions, no izomerization to VIIa could be detected.

Oxidation of the iron carbonyl complexes with cupric bromide

A mixture of VIIa (1.10 g, 3.01 mmol) and $CuBr_2$ (1.68 g, 7.51 mmol) in 25 ml of benzene was stirred magnetically at room temperature for 11 h, during which gas evolution took place. Additional benzene (25 ml) was added, and the solution washed with water until the washings were colorless. The organic phase was dried over Na_2SO_4, and concentrated under vacuum, to yield 0.483 g (43.8%) of IIIa, pure from NMR.

The oxidation of VIIIa and VIIIb was performed similarly, and yielded IVa and IVb in 88% yield. In one preliminary experiment, a dibromo ester (IX) was also obtained in low yield in addition to IIIa. The same product was obtained by treatment of IIIa with $CuBr_2$ in the same conditions, the yield being 7% after 2 h and 10% after 26 h.

Oxidation of the iron carbonyl complexes with ceric ammonium nitrate

In a typical experiment, a saturated solution of $(NH_4)_2[Ce(NO_3)_6]$ was added dropwise with stirring to a solution of 1.142 g of VIIIb in 10 ml of methanol. After standing for 20 min, the mixture was concentrated under vacuum, and the residue was extracted with hexanes. Concentration of this extract under vacuum yielded 0.469 g (81.6%) of IVb, pure from NMR. The oxidation reactions of VIIIa and VIIa were carried out as above yielding pure samples of IVa and IIIa with similar yields.

Synthesis of VIIIa-d_2

A solution of VIII (1.01 g, 5.12 mmol) and sodium ethoxide (0.168 g) in 25 ml C_2H_5OD was allowed to stand under nitrogen at room temperature for 30 min, acidified with 0.25 ml of 38% DCl in D_2O, and concentrated under vacuum. The residue was washed with two 15 ml portions of CH_2Cl_2, which was concentrated under vacuum. The residue was extracted with two 25 ml portions of hexanes, which was concentrated and yielded 0.995 g of Feist's diethyl ester which was 10% VIIIa and 90% VIIIa-d_2 from NMR analysis.

(Methyl acrylate)iron tetracarbonyl

A mixture of 4.01 g of $Fe_2(CO)_9$ and 100 ml of methyl acrylate was stirred at 40-42° under nitrogen for 50 min. After filtration, the solution was concentrated under vacuum, and yielded 2.26 g (81.1%) of a dark oil which crystallized upon standing in the cold. The light yellow crystals melted at 29° (lit. [10] m.p. 28-28.5°); PMR ($CDCl_3$): methyl acrylate: 3.71 (s, CH_3), and 5.82, 6.13 and 6.36 ppm for the *trans*-β,α, and *cis*-β vinylic protons respectively. The coupling constants were $J(\alpha, trans\ \beta)$ 10.5 Hz, $J(\alpha, cis\ \beta)$ 18.0 Hz and $J(cis\ \beta, trans\ \beta)$ 1.5 Hz: (methyl acrylate)iron tetracarbonyl: 3.68 (s, CH_3), 2.60 (d, J 7.5 Hz), 2.91 (d,

J 11.1 Hz) and 3.19 ppm (d,d, J 7.5 and 11.1 Hz) for the *trans*-β and *cis*-β,α vinylic protons respectively. The line broadening in the signals for the β-protons suggested a geminal coupling constant in the order of 2 Hz. These two PMR spectra were first order when measured at 270 Mz, on a Bruker instrument (we are indebted to Dr. Peter P. Fu for these measurments).

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