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REGIOSELECTIVE ALKYLATION AND ACYLATION OF CARBOHYDRATES ENGAGED IN METAL COMPLEXES

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ABSTRACT

Substituted carbohydrate derivatives (D-*gluco*, D-*manno*, and D-*galacto*) having two free hydroxyl groups were converted into their metal chelates by reaction with sodium hydride and a metal chloride (cupric or mercuric) in either oxolane or 1,2-dimethoxyethane. Reaction of these metal chelates with allyl, benzyl, or methyl iodide, or acetic anhydride or benzoyl chloride, gave a mixture of di-, mono-, and un-substituted products in which one monosubstituted derivative preponderated. In the alkylation of copper chelates, disubstitution was absent. Appropriate choice of metal ion and organic reagent often permits selective substitution on either of two hydroxyl groups. Products were separated by liquid chromatography, and characterized by ^{1}H- and ^{13}C-n.m.r. spectroscopy.

INTRODUCTION

In order to explore the significance of oligosaccharides in information-carrying functions and as recognition symbols in physiological processes, it is important to be able to synthesize complex oligosaccharides at will. The synthesis involves two major problems: the formation of glycosidic linkages having high stereoregularity at C-1 of one aldose and complete regioselectivity at a specific hydroxyl group of another. The recent syntheses of a large number of complex oligosaccharides suggest that many of the problems in glycoside-forming reactions have now been solved and that the rate-limiting difficulties often involve regioselective reaction on a specific hydroxyl group, which is usually accomplished by selective protection of multiple hydroxyl groups.

The regioselective blocking-reactions most widely used are those that depend on a choice between axial and equatorial hydroxyl groups (the orthoester[1] and the dibutylstannylene oxide methods[2]), those that selectively convert the most acidic hydroxyl group into an anion for etherification (phase-transfer catalysis[3]), and those that use sterically hindered or less reactive reagents (trityl halides and acyl imidazoles[4]). Ogawa and Matsui[5] also introduced selective activation of an equatorial, secondary hydroxyl group adjacent to an axial hydroxyl group by means of bis(tributylstannylene) oxide.

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A more striking example of regioselective blocking has been demonstrated by Avela *et al.*[6], who investigated the selective substitution of one of two vicinal equatorial hydroxyl groups *via* metal chelates. They showed that copper chelates of the dianions of methyl 4,6-*O*-benzylidene-α- and -β-D-glucopyranoside react with an excess of methyl iodide to give preferential monosubstitution of O-3. They also showed that copper chelates of methyl 2,3-di-*O*-benzyl-D-glucopyranoside can be selectively methylated at either O-4 or O-6, depending on the molar ratio of reagents. In addition, Avela's group reported briefly on the use of other transition metals, and selective acylation and alkylation of sucrose[6d].

In a preliminary communication[7], we reported that Avela's approach using copper chelates may be applied with some generality to the regioselective alkylation (methyl, benzyl, and allyl) of carbohydrate diols. We now describe the use of both copper and mercury chelates for regioselective alkylation and acylation.

RESULTS AND DISCUSSION

The initial work by Avela *et al.*[6] showed that copper chelates of carbohydrate vicinal diols, prepared from a sugar, sodium hydride, and a metal chloride in the molar ratios of 1:2:1, are more regioselective in methylation than any other chelates they investigated. Our initial experiments using methyl iodide with 1:2:1 complexes confirmed their findings and indicated that regioselectivity could be extended to other carbohydrate derivatives.

It was found that carbohydrate derivatives having vicinal hydroxyl groups (*e,e* or *a,e*), or those having O-4 and O-6 free, were able to form 1:2:1 copper complexes. All of the complexes were soluble in oxolane (THF) or 1,2-dimethoxyethane (DME), and afforded dark-green solutions. Other colors, usually blue, indicated that 1:2:1 complexes had not been formed, and the ratios of products obtained from those reactions were not reproducible. In scaling-up the reactions, it is also very important to increase the proportion of solvent used. For example, methyl 4,6-di-*O*-benzyl-α-D-mannopyranoside (3.0 g) failed to give the 1:2:1 complex when dissolved in 50 mL of THF, but, when the reaction was repeated using 150 mL of solvent, the green 1:2:1 complex was formed.

To make the alkylation technique more applicable to the synthesis of derivatives having persistent and temporary blocking-groups, we investigated the reaction of benzyl and allyl halides, rather than methyl iodide, with these copper complexes. The alkyl chlorides showed no reaction, and the alkyl bromides gave a yield of <20% of alkylated products in a reasonable time. However, when the alkyl iodides were used, selective alkylation occurred that equalled the selectivity reported for methyl iodide, and yields of alkylation products isolated were generally >85%. The results of these reactions are shown in Table I.

In almost every instance, the yield of monosubstituted product was >85%, the rest being accounted for as unreacted starting-material. In no case was any disubstituted product isolated. Of the monosubstituted products, the alkylation was

TABLE I

ALKYLATION OF 1:2:1 METAL COMPLEXES OF CARBOHYDRATES

Compound alkylated[a]	*Solvent*	*Metal*	*Alkyl iodide*	*Composition (%)*			
				2	*3*	*2,3*	*A*[b]
Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside[8–10]	THF	Cu	methyl	20	66	—	14
	DME	Cu	benzyl	18	74	—	8
	DME	Hg	benzyl	20	16	49	15
	DME	Cu	allyl	19	77	—	4
Methyl 4,6-*O*-benzylidene-α-D-mannopyranoside[11,9,10]	DME	Cu	allyl	19	81	—	—*
	THF	Cu	allyl	20	80	—	—*
Methyl 4,6-di-*O*-benzyl-α-D-mannopyranoside[7]	DME	Cu	allyl	19	76	—	5
	THF	Cu	benzyl	15	85	—	—*
	DME[c]	Cu	benzyl	—	95	—	5*
	DME	Hg	benzyl	38	22	19	21
Methyl 4,6-*O*-ethylidene-α-D-glucopyranoside[12]	DME	Cu	allyl	23	77	—	—
	THF	Cu	allyl	20	80	—	—*
	DME	Cu	benzyl	32	68	—	—
Methyl 4,6-*O*-benzylidene-α-D-galactopyranoside[13]	DME	Cu	allyl	29	68	—	—
	DME	Cu	benzyl	29	68	—	—
1,6-Anhydro-4-*O*-benzyl-β-D-mannopyranose[14]	DME	Cu	benzyl	36	64	—	—
				4	*6*	*4,6*	*A*
Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[15]	DME	Cu	allyl	61	15	—	24
	THF	Cu	allyl	36	31	—	33
	DME	Cu	benzyl	51	25	—	24
Methyl 2,3-*O*-isopropylidene-α-D-mannopyranoside[16,17]	THF	Cu	methyl	100	—	—	—*
	DME	Cu	allyl	78	10	—	12
	THF	Cu	allyl	100	—	—	—*
	DME	Cu	benzyl	75	19	—	6
	THF	Cu	benzyl	100	—	—	—*
Methyl 2,3-di-*O*-benzyl-α-D-galactopyranoside[18]	DME	Cu	allyl	70	26	—	4
	DME	Cu	benzyl[c]	63	33	—	4
				3	*4*	*3,4*	*A*
1,6-Anhydro-2-*O*-benzyl-β-D-galactopyranose[19]	DME	Cu	benzyl	—	91	—	9*
Methyl 2,6-di-*O*-benzyl-α-D-galactopyranoside[20]	DME	Cu	allyl	55	22	—	23
	DME	Cu	benzyl	48	29	—	23
				5	*6*	*5,6*	*A*
3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose[21]	DME	Cu	allyl	50	40	—	10
	DME	Cu	benzyl	48	40	12	—
				2	*6*	*2,6*	*A*
Methyl 3,4-*O*-isopropylidene-α-D-galactopyranoside[22]	DME	Cu	benzyl	35	34	—	31
				1	*2*	*1,2*	*A*
3,4,6-Tri-*O*-benzyl-D-glucopyranose[23]	DME	Cu	allyl	—	—	—	100

[a]First reference is to synthesis, and the following to the ^{13}C-n.m.r. spectrum. Reactions of special synthetic interest are indicated by an asterisk. [b]Starting material. [c]Correction of preliminary communication[7].

at the less acidic hydroxyl group, that is, O-3 in preference to O-2, and O-4 in preference to O-6. Apparently, the copper complex deactivates the dianion, making both oxygen atoms less nucleophilic, and the need to use the (more reactive) alkyl iodides supports this conclusion. The more acidic hydroxyl group must generate an anion that bonds more tightly with copper, making its electrons less available for nucleophilic attack on iodide. Thus, the less acidic hydroxyl group becomes the more nucleophilic anion, and reacts preferentially. Although both anions generally reacted to differing degrees, no disubstitution was observed. Thus, monoalkylation, and the formation of one copper–iodide bond, must further decrease the reactivity of the second anion, unless the effect is purely physical. In general, precipitation occurred after monosubstitution, and this may have isolated the reactants. In 3,4,6-tri-*O*-benzyl-D-glucopyranose, both of the free hydroxyl groups are relatively more acidic, and both anions are deactivated to such a degree that neither reacts with the alkyl iodide. 3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose displayed little regioselection upon alkylation, perhaps because of inadequate difference in acidity.

Variations in the structure of the carbohydrate derivative, including the configuration of the parent sugar, its anomeric form, and the substituent groups, also exert an effect on the regioselectivity. Avela *et al.*[6a,b] showed that 1:2:1 copper complexes of methyl α- and β-D-glucopyranoside differ in regioselectivity upon alkylation. We have also found that the use of different blocking groups, such as isopropylidene or benzylidene, instead of di-*O*-benzyl, can cause large changes in the regioselection. There does not appear to be any clear correlation thus far recognizable between types of blocking groups and regioselectivity.

Solvent also has an effect on the regioselectivity of alkylation. This is not surprising, as the metal complexes are coordinated to solvent molecules as well as to the oxygen anions. Only two solvents, THF and DME, were investigated (see Table I), and their effect on regioselectivity was variable. The influence of solvent on regioselectivity is not yet predictable, but solvent selection is clearly a useful experimental variable.

Carbohydrate diols can also form 1:2:1 chelates with mercuric chloride. These chelates are soluble in such solvents as THF or DME, and usually give colorless or yellow solutions. Alkylation of a number of these complexes produced no regioselectivity and gave appreciable proportions of disubstituted products. The mercury chelates apparently have less deactivating effect on the anions, owing to weaker metal–oxygen bonds.

Avela and co-workers[6d–f] reported that metal complexes can also be used for regioselective acylation. The metal complexes of sucrose and methyl 4,6-*O*-benzylidene-α-D-glucopyranoside were treated with various acid chlorides or anhydrides to give mixtures of acylated products in which monoacylation predominated. In Table II are shown the results of our investigation of the acylation of 1:2:1 mercury and copper chelates. Acetylation of the carbohydrate derivatives with one molar proportion of acetic anhydride in pyridine was used for comparison.

TABLE II

ACYLATION OF CARBOHYDRATES

Compound alkylated[a]	*Metal*[b]	*Ratios*[c]	*Acyl group*	*Composition (%)*[d]			
				2	*3*	*2,3*	*A*[e]
Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside	—	1:0:1	acetyl	24	52	21[24]	3
	Hg	1:1:2	acetyl	82	—	18	—*
	Cu	1:1:2	acetyl	15	80	5	—
	Hg	1:1:2	benzoyl	87	—	13[24]	—*
Methyl 4,6-*O*-benzylidene-α-D-mannopyranoside	—	1:0:1	acetyl	—	50	39[24]	11
	Hg	1:1:2	acetyl	38	21	41	—
	Hg	1:1:2	benzoyl	25[25]	18	57[24]	—
Methyl 4,6-di-*O*-benzyl-α-D-mannopyranoside	—	1:0:1	acetyl	7	47	23	23
	Hg	1:1:2	acetyl	61	23	—	16
	Hg	1:1:2	acetyl	77	11	4	9*
	Cu	1:1:2	acetyl	10	65	—	25
	Hg	1:1:2	benzoyl	50	21	29	—
	Cu	1:1:2	benzoyl	25	75	—	—
Methyl 4,6-*O*-ethylidene-α-D-glucopyranoside	—	1:0:1	acetyl	26	31	21	22
	Hg	1:1:2	acetyl	52	—	48	—
	Cu	1:1:2	acetyl	28	31	41	—
	Hg	1:1:2	benzoyl	60	—	40	—
	Hg	1:2:2	acetyl	25	—	75	—
	Hg	1:1:1.2	benzoyl	40	54	6	—
1,6-Anhydro-4-*O*-benzyl-β-D-mannopyranose	—	1:0:1	acetyl	27	51	11	11
	Hg	1:1:2	acetyl	19	42	39	—
	Cu	1:1:2	acetyl	26	64	10	—
Methyl 4,6-*O*-isopropylidene-α-D-galactopyranoside[26]	Hg	1:1:2	acetyl	64	2	34	—
	Hg	1:1:2	benzoyl	48	19	33	—
				4	*6*	*4,6*	*A*
Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside	—	1:0:1	acetyl	12	59[27]	12[27]	17
	Hg	1:1:2	acetyl	—	89	11	—*
	Cu	1:1:2	acetyl	13	68	19	—
	Hg	1:1:2	benzoyl	—	88[10]	12	—*
	Hg	1:1:1.2	benzoyl	—	90	—	10*
Methyl 2,3-*O*-isopropylidene-α-D-mannopyranoside	—	1:0:1	acetyl	10	50	18[28]	22
	Hg	1:1:2	acetyl	—	89	11	—*
	Cu	1:1:2	acetyl	5	51	44	—
	Hg	1:1:2	benzoyl	—	70	30	—
	Hg	1:1:1.2	benzoyl	—	79	21	—*
				3	*4*	*3,4*	*A*
Methyl 2,6-di-*O*-benzyl-α-D-galactopyranoside	—	1:0:1	acetyl	73	—	14	—
	Hg	1:1:2	acetyl	68	—	2	30
	Cu	1:1:2	acetyl	58	3	—	39
	Hg	1:1:2	benzoyl	77	—	—	23*

[a]Reference is to synthesis. [b]No metal mentioned indicates reaction done in pyridine. [c]Molar ratios of sugar:metal:acylating agent. [d]Reference is to the literature reporting the ^{1}H-n.m.r. spectrum. Reactions of special synthetic interest are indicated by an asterisk. [e]Starting material.

The reaction of the acylating reagent with the metal chelates was very rapid. Most reactions with the mercury complexes were complete within 5 to 10 min. The copper chelates reacted more slowly, but the reaction was complete within one hour. The corresponding acylations in pyridine required almost 48 h to proceed to completion. The ratio of products obtained from the acylation of the metal complexes was the same, regardless of whether the acylating agent was an acid chloride or an acid anhydride.

In general, the metal complexes gave monoacylated derivatives as the major product, although disubstituted products were also formed in significant proportions. The mercury complexes usually favored regioselection of the more acidic hydroxyl group, whereas the behavior of the copper complexes was less predictable. The regioselectivity differed greatly between different carbohydrate derivatives, and prediction of the outcome of a particular reaction was not possible.

The initial reactions were conducted with two molar proportions of the acylating agent, to make certain that the metal complex was directing the course of the reaction. The greater reactivity of the acylating agent, and its presence in excess, caused the formation of disubstituted products. When 1.2 mol. equiv. of the acylating reagent were used, the amount of disubstitution decreased significantly. With methyl 4,6-*O*-ethylidene-α-D-glucopyranoside, no product monoacylated at O-3 was found, although disubstitution occurred. When only 1.2 mol of the acylating reagent was used, both the O-2 and O-3 monoacylated derivatives were formed, and only a small amount of disubstitution occurred. Acylation of the mercury complex at O-3 must make the remaining O-2–Hg bond more nucleophilic, so that it then reacts with the excess of the acylating agent to form the disubstituted product.

The high rate and the regioselectivity of acylation of mercury complexes provide, in some cases, a better alternative route to monoacylation than standard phase-transfer reactions, although, in general, the selectivity is less than in the alkylation of copper complexes. Recently, we reported[29] the use of a mercury complex in the synthesis of 2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranoside derivatives in 80% yield, with a reaction time of 1 h. Methods of acylation and alkylation of both copper and mercury complexes that appear to have especial synthetic promise are marked with an asterisk in Tables I and II.

In summary, substitution on metal chelates of carbohydrate dianions provides an experimentally simple method for selectively protecting either one of two hydroxyl groups in a number of organic compounds. The method can serve as an attractive alternative to the dibutylstannylene and phase-transfer methods.

EXPERIMENTAL

General methods. — ^{1}H-N.m.r. spectra were recorded with a Varian EM-360 or XL-100-15 spectrometer, and ^{13}C-n.m.r. spectra with a Varian XL-100-15 or CTF-20 spectrometer, for solutions in chloroform-*d*, with tetramethylsilane as the

internal reference. For liquid chromatography (l.c.), an apparatus equipped with a Glenco model HPLPS-1 pump, a Valco injector, a Waters differential refractometer R-401, a Waters u.v. detector (254 nm), and a Whatman Partisil M9 10/25 column was used at a flow rate of 8.0 mL/min and a pressure of ~10.4 MPa.

Oxolane (THF) and 1,2-dimethoxyethane (DME) were refluxed over lithium aluminum hydride, distilled, and stored over calcium hydride. The solvents were distilled before use. Cupric and mercuric chlorides were dried at 100° *in vacuo* before use. Benzyl iodide was prepared from benzyl chloride and sodium iodide in acetone. Benzyl, allyl, and methyl iodides were distilled, and stored over copper turnings. Acetic anhydride and benzoyl chloride were distilled before use.

Alkylation of carbohydrate–metal chelates. — The carbohydrate derivative having two free hydroxyl groups (0.5 g) was treated with sodium hydride (2+ equiv., 57% in mineral oil) in dry DME (25 mL). After the evolution of hydrogen had ceased, anhydrous metal(II) chloride ($CuCl_2$ or $HgCl_2$, 1 mol. equiv.) was added. After 5 to 30 min, the evolution of hydrogen ceased, the metal halide had dissolved completely, and a clear, green solution for the copper chelates, and a colorless to yellow solution for the mercuric chelates, resulted. Alkyl iodide (5 equiv.) was added, and the mixture was boiled under reflux for 24 h. During this time, the solutions became colorless and a precipitate formed. The mixtures were cooled, treated with ammonium hydroxide (4 mL, for the copper reactions only) and water, and evaporated to dryness. Further additions of water were evaporated from the products to remove most of the unreacted alkyl iodide. The residue was dissolved in ethyl acetate, and the solution washed: for copper chelates, with dilute ammonium hydroxide until the aqueous layer was colorless, or, for mercury chelates, with distilled water. The aqueous layers were combined, and made weakly acidic with M hydrochloric acid; sodium chloride and sodium thiosulfate were added, and the solution was extracted with ethyl acetate. The extracts were combined, washed with water, dried (sodium sulfate), and evaporated to a syrup. The crude products were separated, by l.c. with 1:2 (v/v) ethyl acetate–hexane, into 4 or 5 fractions. Fraction 1 contained mineral oil, alkyl iodide, and solvents; fraction 2, any dialkylated product; fraction 3 or 4, or both, the monosubstituted derivatives; and fraction 4 or 5, the starting material. The weight of each fraction was determined, and the ratio of the monosubstituted products was calculated from peak areas in the ^{13}C-n.m.r. spectrum. Ratios were checked by comparison of peak areas in the liquid chromatograms, and by the weights of resolved fractions. The results are given in Table I.

Acetylations in pyridine. — The partially protected carbohydrate derivative (1.0 mmol) having two free hydroxyl groups was dissolved in dry THF (10 mL) and pyridine (3–5 mL) at room temperature. Acetic anhydride (1.0 mmol) was added, and the solution was stirred until the reaction was complete, as shown by t.l.c. (~40 h). A few drops of water were added, and the mixture was evaporated to a syrup; toluene was then added and evaporated, to remove the last traces of pyridine and acetic acid. The crude product was separated into four fractions by l.c.

using 1:1 (v/v) ethyl acetate–hexane as the eluant. Fraction 1 contained solvents; fraction 2, the diacetylated products; fraction 3, the monoacetylated products; and fraction 4, the starting material. Each fraction was evaporated, and the material weighed in order to determine the yield. The ratio of monoacetylated products in fraction 2 was determined from the ^{1}H- or the ^{13}C-n.m.r. spectrum, or both.

Acylation of carbohydrate–metal chelates. — To a solution of the carbohydrate diol derivative (1.0 mmol) in dry THF (10 mL) was added sodium hydride (2.1 mmol, 50% in mineral oil), and the mixture was stirred at room temperature until the evolution of hydrogen ceased. Anhydrous metal(II) chloride ($CuCl_2$ or $HgCl_2$; 1.0 mmol) was added, and the mixture was stirred until all of the metal salt had dissolved and reacted (15–30 min). The acylating agent (1 or 2 mmol) was added, and, after 1 h, water (2 mL) and acetic acid (1 to 2 drops) were added. The solution was evaporated, the crude product dissolved in dichloromethane, the solution washed successively with water, aqueous sodium hydrogencarbonate, and saturated sodium chloride solution, dried (sodium sulfate), and evaporated to a syrup or a solid. The products were separated and identified as already described.

Identification of products from their n.m.r. spectra. — The identity of the acylated products was, in most cases, determined from their ^{1}H-n.m.r. spectra. Such spectra of some of the products were found in the literature (see Table II), and identification was made by direct comparison. Disubstituted products were identified on the basis of integration data, and, in most instances involving acetates, by the presence of two acetyl methyls (δ 2.0). The position of the acyl group in the monoacyl derivatives was established by the coupling constants of the proton attached to the carbon atom bearing the acyloxy group. In general, antiparallel disposition (*a–a*) gave rise to large coupling constants (9–10 Hz), whereas those in *gauche* disposition gave smaller values (1–2 Hz for *e–e*, and 2.2–3.5 Hz for *a–e*)[30,31]. In most cases, the signal of the proton (H-2, H-3, and H-4) on a carbon atom bearing an acyloxy group could be located in the region of δ 3.8 to 5.7, and it was usually free from overlap with the signals of other protons. Thus, identification of 2-*O*-, 3-*O*-, and 4-*O*-acyl products was usually straightforward. Identification of a 6-*O*-substituted derivative was made by eliminating the possibility that it was 4-*O*-substituted (lack of any proton in the δ 3.8–5.8 region) and from its ^{13}C-n.m.r. spectrum.

The identity of a disubstituted, alkylated product was usually determined by integration of its ^{1}H-n.m.r. spectrum. For the monosubstituted alkyl derivatives, ^{13}C-n.m.r. spectroscopy proved to be the better method. The assignment of carbon atoms in the starting materials was determined from literature values, or by comparison with model compounds. Assignments of carbon atoms and position of the alkyl group were made by comparing the spectrum of the product with that of the starting material, and applying the general rules[13,32] that alkyl substitution of a hydroxyl group causes a 6–9 p.p.m. downfield shift for the alpha carbon atom (3–4 p.p.m. if the hydroxyl group is axial), a 2-p.p.m. upfield shift for the beta carbon atom, and a zero or small upfield shift for the gamma carbon atom.

For example, the shift of the signal of C-1 can be used to determine whether the substitution is at O-2 or O-3. If the C-1 signal shifts upfield, substitution is at O-2, whereas, if C-1 is found to have the same, or a slightly downfield, chemical shift, the substitution is at O-3. The shift, or lack of shift, of the C-6 signal may similarly be used to determine if substitution occurred at O-6 or O-4.

Where a l.c. fraction contained both monosubstituted products, the ratio was determined from the ratio of the peak heights of the same carbon atom in each compound. For example, the ratio of peak heights of C-1 was used to determine the molar ratio of O-2 to O-3 substitution. Comparisons of other peak heights, such as those of C-4, of methyl carbons in *O*-methyl substitution, and of the terminal alkene carbon atom in the allyl group, were used as checks on the ratio of isomers.

^{13}C-N.m.r. spectroscopy was also used to determine the structure of monoacylated products, by employing the techniques already described for the alkylated products. In general, acylation causes a downfield shift of the signal of the alpha carbon atom (1–2 p.p.m., although the shift can be quite variable), a 1.5–3-p.p.m. upfield shift for that of the beta carbon atom and a small, or zero, downfield shift for that of the gamma carbon.

Over 60 compounds were synthesized during this study, and lack of space does not allow a complete listing of the ^{1}H- or ^{13}C-n.m.r. data for each compound. The data will, however, be made available to anyone who requests them.

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