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STEREOSELECTIVE SYNTHESES OF *C*-(D-GLUCOPYRANOSYL)ALKENES*

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ABSTRACT

α-D-Glucopyranose pentaacetate (**1**) was found to undergo stereoselective conversion in good yield into 3-(tetra-*O*-acetyl-α-D-glucopyranosyl)-1-propene (**4**) by treatment with allyltrimethylsilane and boron trifluoride etherate in acetonitrile. Similar treatment of methyl tetra-*O*-acetyl-α-D-glucopyranoside or tetra-*O*-acetyl-α-D-glucopyranosyl bromide also gave **4** in preference to its β anomer, but net yields were lower. Similar reaction of **1** with (*E*)-penta-2,4-dienyltrimethylsilane afforded the readily polymerizable 5-(tetra-*O*-acetyl-α-D-glucopyranosyl)-(*E*)-1,3-pentadiene, accompanied by a minor proportion of its β anomer.

INTRODUCTION

Lewis *et al.*[2] reported that the reaction of 2,3,4,6-tetra-*O*-benzyl-α-D-glycopyranoses with allyltrimethylsilane and $BF_3 \cdot Et_2O$ gave 3-(α-D-glycopyranosyl)-1-propenes as major products. Kozikowski *et al.*[3] used similar conditions with 4-*O*-*tert*-butyldimethylsilyl-2,3-*O*-cyclohexylidene-L-lyxopyranoses and obtained principally *C*-α-lyxopyranosyl derivatives. Acton *et al.*[4] reported that a protected daunosamine derivative gave the *C*-α-glycopyranosyl derivative as the only product under similar conditions.

All of these reactions were performed at a moderate temperature (0° to room temperature) with starting compounds having nonparticipating groups at C-2, and were explained as proceeding *via* formation of ring oxonium ions. Protection by ester groups can be expected to greatly affect the outcome of the reaction; under comparable reaction conditions 1,2,3,4-tetra-*O*-benzoyl-L-lyxopyranose gave[3] a 1:5 mixture of *C*-α- and β-lyxopyranosyl derivatives. In the acetylated D-glucopyranose structure it would be expected, as established by Paulsen[5], that an initial oxonium ion arising by loss of the 1-acetoxy group would readily undergo a sequence of rearrangements *via* cyclic acetoxonium ions through participation of suitably

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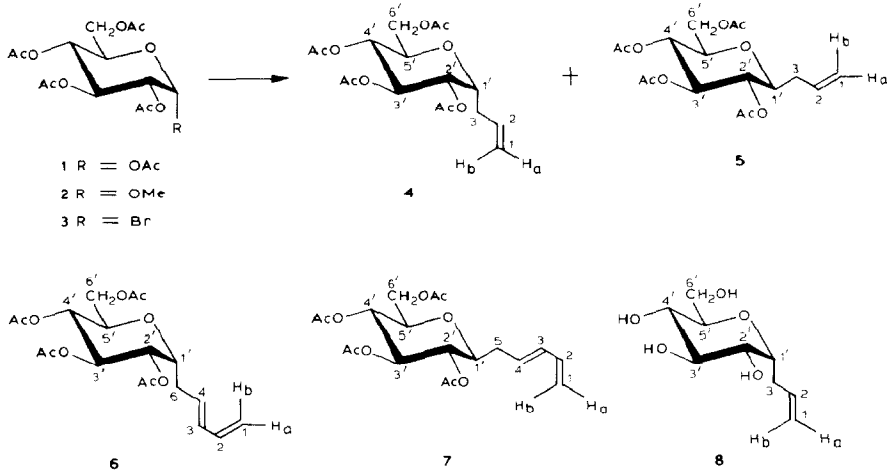

disposed *O*-acetyl groups at C-2, -3, -4, and -6. In the light of such considerations, the behavior that we observed in the reaction of D-glucopyranose pentaacetate with allyltrimethylsilane to give primarily the *C*-α-glycosyl derivative appeared exceptional and of synthetic interest.

RESULTS AND DISCUSSION

α-D-Glucopyranose pentaacetate (**1**) was treated with allyltrimethylsilane (10 mol.equiv.) and $BF_3{\cdot}Et_2O$ (10 mol. equiv.) in dry acetonitrile for 8 h at 80° under nitrogen. Purification on a column of silica gel gave a 5:1 mixture of peracetylated 3-(α-and β-D-glucopyranosyl)-1-propenes (**4** and **5**) in 64% combined yield, the α anomer thus strongly preponderating despite the presence of the 2-*O*-acetyl group. Recrystallization of the mixture from chloroform–hexane gave pure **4** as needles in 45% yield. The product was dextrorotatory ($[\alpha]_D$ +72° in chloroform) and the preparation was readily conducted on a multi-gram scale. Catalytic *O*-deacetylation of **4** gave the crystalline, dextrorotatory 3-(α-D-glucopyranosyl)-1-propene (**8**) in quantitative yield.

When α-D-glucopyranose pentaacetate (**1**) in acetonitrile was treated with 10 mol. equiv. of allyltrimethylsilane and only 1–2 mol. equiv. of $BF_3{\cdot}Et_2O$ at room temperature, no reaction occurred, even after several days. Elevation of the temperature to 80° led to slow reaction; after 4 days, one half of the starting compound **1** still remained and the transformed product was a mixture of **4** and **5**. Evidently, the use of a large excess of $BF_3{\cdot}Et_2O$ kept the reaction period short and gave a product-mixture in which the α anomer was strongly favored.

A report by Tsunoda *et al.*[6] described the conversion of 2-methoxytetrahydro-2*H*-pyran into its 2-allyl analog in 78% yield by the action of allyltrimethylsilane and trimethylsilyl triflate. The same reagents were used by Hosomi *et al.*[7] with

methyl tetra-*O*-benzyl-α-D-glucopyranoside to give a mixture of 1-*C*-allyl derivatives with the α anomer strongly preponderating. Accordingly, based on these examples, methyl tetra-*O*-acetyl-α-D-glucopyranoside (**2**) was treated for 2 days by the procedure described for **1**. A 5:1 mixture of *C*-glycosyl derivatives **4** and **5** was obtained, but in only 23% combined yield. Likewise, tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**3**) was evaluated as a possible starting compound; a 5:1 mixture of **4** and **5** was isolated, but in only 15% combined yield.

To consolidate the structural attributions for compounds **4** and **5**, an authentic sample of the β anomer **5** was prepared from the glycosyl halide **3** by a modification of the method report by Shulman *et al.*[8]. Treatment of **3** with an excess of allylmagnesium bromide in dry oxolane–ether under nitrogen, followed by acetylation, gave the crystalline, weakly levorotatory compound **5**, although only in 25% yield. The ^{1}H- and ^{13}C-n.m.r. spectra of **4** and **5** (Tables I–III) were analyzed in detail to establish the assigned structures.

The ^{1}H-n.m.r. spectrum of **4** showed an apparent quintet (ddd,*J* 4.8, 5.8, 10.5 Hz) for H-1′ at δ 4.28 and a doublet of doublets (*J* 5.8, 9.0 Hz) for H-2′ at δ 5.08 having $J_{1',2'}$ 5.8 Hz. In contrast, the ^{1}H-n.m.r. spectrum of **5** showed a doubled doublet of doublets (*J* 4.2, 7.0, 9.5 Hz) for H-1′ at δ 3.50 and a triplet (*J* 9.5 Hz) for H-2′ at δ 4.92 having $J_{1',2'}$ 9.5 Hz. In line with expectations, the signal of the axially oriented H-1′ of **5** resonates at higher field than the equatorially oriented H-1′ of **2**, and the $J_{1',2'}$ value of **5** is larger than that of **4**. The large values of $J_{2',3'}$, $J_{3',4'}$, and $J_{4',5'}$ (9.0 Hz for **4**, 9.5 Hz for **5**) confirmed that the two products retained the D-*gluco* configuration and the pyranose ring.

The ^{13}C-n.m.r. spectra (Table III) showed the C-1′ signals of **4** and **5** at δ 71.97 with $^1J_{C,H}$ 151 Hz and δ 77.28 with $^1J_{C,H}$ 143 Hz, respectively. Bock *et al.*[9] reported that α-glycose and α-glycoside derivatives had larger $^1J_{C,H}$ values at C-1′ than the corresponding β anomers. The present results are in accord with this correlation and demonstrate the utility of determining $^1J_{C,H}$ values at C-1′ for establishing the configuration at C-1′ of *C*-glycopyranosyl derivatives.

The foregoing work furnishes a *C*-α-glucosylalkene for studies as a potential dienophile in cycloaddition reactions[10]. In an effort to obtain a corresponding *C*-α-glucosylalkadiene that could react with an external dienophile, α-D-glucopyranose pentaacetate (**1**) was treated with (*E*)-2,4-pentadienyltrimethylsilane[11] in acetonitrile in the presence of $BF_3{\cdot}Et_2O$. The reaction gave a 4:1 mixture of the 5-(α- and β-D-glucopyranosyl)-(*E*)-1,3-pentadiene derivatives **6** and **7** in 33% combined yield as a syrup, after purification on a column of silica gel. The ^{1}H-chemical shifts and spin couplings determined (Tables I and II) for each compound (from the mixture) are similar to those of **2** and **3**, except for the signals of H-2 and H-3. Comparison of the ^{1}H-chemical shifts of H-1′ and $J_{1',2'}$ values for such *C*-glucopyranosyl derivatives are thus very useful for determining configurations at C-1′. The $J_{3,4}$ values of **6** and **7** were 15.0 Hz, thus establishing that they were the *E*-isomers. This mixture of dienes was unstable and polymerized readily at room temperature.

The observed course of the reactions described here suggests that the highly

TABLE I

^{1}H-N.M.R. CHEMICAL SHIFTS (δ) AND SIGNAL MULTIPLICITIES OF 3-(TETRA-*O*-ACETYL-α-D-GLUCOPYRANOSYL)-1-PROPENE[a] (**4**), ITS β ANOMER[a] **5**, 5-(TETRA-*O*-ACETYL-α-D-GLUCOPYRANOSYL)-(*E*)-1,3-PENTADIENE[b] (**6**), AND ITS β ANOMER[b] **7** IN $CDCl_3$

Compound	*H-1a*	*H-1b*	*H-2*	*H-3a*	*H-3b*	*H-4*	*H-5a*	*H-5b*	*H-1'*	*H-2'*	*H-3'*	*H-4'*	*H-5'*	*H-6'a*	*H-6'b*	*Ac*
4	5.12 dq	5.16 dq	5.76 dddd	2.35 dddt	2.56 dddt				4.28 ddd[c]	5.08 dd	5.34 t	4.98 t	3.87 ddd	4.08 dd	4.21 dd	2.03, 2.04, 2.05, 2.07
5	—— 5.07 ——		5.82 ddt	2.27 dtt	2.33 dddt				3.50 ddd	4.92 t	5.17 t	5.05 t	3.63 ddd	4.10 dd	4.23 dd	1.99, 2.018, 2.023, 2.07
6	5.02	5.12	6.30 dt	6.14 broad dd		5.61 dt	2.36 ddd	2.57 ddd	4.27 ddd[c]	5.08 dd	5.33 t	4.95 t	3.85 ddd	4.07 dd	4.18 dd	2.02, 2.03 (2Ac), 2.04
7	5.02	5.13	6.29 dt	6.01 broad dd		5.66 dt	—— 2.32 ——		3.48 ddd	4.90 t	5.16 t	5.03 t	3.62 ddd	4.09 dd	4.22 dd	1.98, 1.998, 2.004, 2.06

[a]At 500 MHz. [b]At 200 MHz. [c]Apparent quintet.

TABLE II

FIRST-ORDER ^1H–^1H COUPLING CONSTANTS (Hz) OF 3-(TETRA-*O*-ACETYL-α-D-GLUCANOPYRANOSYL)-1-PROPENE (**4**) AND ITS β ANOMER **5**, AND OF 5-(TETRA-*O*-ACETYL-α-D-GLUCOPYRANOSYL)-(*E*)-1,3-PENTADIENE (**6**) AND ITS β ANOMER **7** IN $CDCl_3$[a]

Compound	$J_{1a,1b}$	$J_{1a,2}$	$J_{1b,2}$	$J_{1a,3a}$	$J_{1a,3b}$	$J_{1b,3a}$	$J_{1b,3b}$	$J_{2,3a}$	$J_{2,3b}$	$J_{3a,3b}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5b}$	$J_{5a,5b}$
4	~1	10	17	~1	~1	~1	~1	6.0	7.5	15.5				
5		10	18	~1	~1	~1	~	7.0	7.0	15				
6		10	16.5						10.0		15.0	7.0	7.0	15.5
7		10	16.5						10.0		15.0	7.0	7.0	

Compound	$J_{3a,1'}$	$J_{3b,1'}$	$J_{5a,1'}$	$J_{5b,1'}$	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'a}$	$J_{5',6'b}$	$J_{6'a,6'b}$
4	4.8	10.5			5.8	9.0	9.0	9.0	2.8	5.2	12.0
5	7.0	4.2			9.5	9.5	9.5	9.5	2.5	5.0	12.2
6			4.8	10.2	5.5	9.2	9.2	9.2	2.5	5.5	12.2
7			4.8	6.5	9.6	9.6	9.6	9.6	2.2	5.0	14.0

[a]At 500 MHz for **4** and **5**; at 200 MHz for **6** and **7**.

TABLE III

^{13}C-N.M.R. CHEMICAL SHIFTS (δ) AND ^{13}C–^{1}H-COUPLING CONSTANTS[a] OF 3-(TETRA-*O*-ACETYL-α-D-GLUCOPYRANOSYL)-1-PROPENE (**4**) AND ITS β ANOMER **5** IN $CDCl_3$ AT 125 MHz

Compound	*C-1*	*C-2*	*C-3*	*C-1'*	*C-2'*	*C-3'*	*C-4'*	*C-5'*	*C-6'*	*CH_3*	*C=O*
4	117.83	133.16	30.63	71.97	70.35	70.43	68.95	68.95	62.32	20.64	169.61
										20.68	169.68
				(151)	(151)	(151)	(148)	(148)	(148)		170.15
											170.66
5	117.68	133.00	35.88	77.28	71.73	74.47	68.76	75.71	62.37	20.60	169.47
										20.63	169.52
				(143)	(151)	(157)	(154)	(144)	(148)	20.72	170.39
											170.64

[a] $^{1}J_{C,H'}$ (Hz) in parentheses.

polar solvent (acetonitrile), in conjunction with the large excess of Lewis acid, leads to initial formation of an open oxonium ion from the starting sugar derivative, despite the presence of a participating group at C-2'. The presence of a high concentration of allyltrimethylsilane from the large excess used then leads to capture of this nucleophile, with a stereoelectronically favored approach from the axial direction, to give the *C*-α-glucosyl product that terminates the reaction before the onset of acyloxonium-ion rearrangements or other competing pathways.

Since the completion of this work[1], several significant papers concerning *C*-glucosylation have been reported. Giannis and Sandhoff[12] reported that the β anomer of **1** can be converted stereoselectively into **4**. Hoffman and Schmidt[13] reported that *O*-benzyl protected α-D-glucopyranosyl trichloroacetimidate was stereoselectively converted into the *O*-benzyl analog of **4** in the presence of zinc chloride as the Lewis acid. Bennek and Gray [14] have demonstrated a high-yielding conversion of methyl α-D-glucopyranoside *via* its per(trimethylsilyl) ether by the action of allyltrimethylsilane in the presence of trimethylsilyl trifluoromethanesulfonate into 3-(α-D-glucopyranosyl)-1-propene (**8**) having a m.p. close to that recorded for **8** in this work, and giving ^{1}H-n.m.r. data for its tetraacetate similar to those recorded here for compound **4**.

EXPERIMENTAL

General methods.— Melting points were determined in open glass capillaries in a Thomas–Hoover apparatus, and are uncorrected. Specific rotations were determined with a Perkin–Elmer Model 141 polarimeter. I.r. spectra were recorded with a Perklin–Elmer 457 grating spectrophotometer. ^{1}H-N.m.r. spectra at 200 and 500 MHz were recorded with Bruker WP-200 and AM-500 spectrometers, respectively. ^{13}C-N.m.r. spectra at 125 MHz were recorded with a Bruker AM-500

instrument. Spectra with the AM-500 instrument at The Ohio State University Instrument Center were recorded by Dr. C. E. Cottrell. All signal assignments were verified by ^{13}C-^{1}H correlation spectra. The $^{1}J_{C,H}$ values were determined by using Bruker's INEPTP.AU microprogram. Tetramethylsilane (δ 0.00) was used as the internal standard. Chemical-ionization (c.i.) mass spectra were recorded by C.R. Weisenberger at The Ohio State University Chemical Instrumentation Center with a Kratos MS-30 mass spectrometer. T.l.c. was performed on precoated plates of Silica gel 60 (E. Merck); components were detected by spraying the plates with 10% H_2SO_4 and subsequent heating. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Georgia.

*3-(Tetra-*O*-acetyl-*α*-*D*-glucopyranosyl)-1-propene* (**4**).—*(a) From* **1**. To a solution of penta-*O*-acetyl-α-D-glucopyranose (**1**, 116 mg, 0.30 mmol) in dry acetonitrile (2.3 mL) was added allyltrimethylsilane (0.47 mL, 3.0 mmol) and $BF_3{\cdot}Et_2O$ (0.37 mL, 3.0 mmol). The mixture was heated for 8 h at 80° under N_2. Evaporation gave a pale-brown syrup which was dissolved in chloroform (2 mL). The solution was washed successively with water, aqueous $NaHCO_3$, and water, dried (Na_2SO_4), and evaporated to give a pale-brown syrup (135 mg), which was purified on a column of silica gel with 4:1 toluene–ethyl acetate. A mixture of **4** and its β anomer **5** (10.0 mg, 9%; α:β = 2:3) was obtained by concentration of faster-eluted fractions, and a mixture of **4** and **5** (61.0 mg, 55%; α:β = 8.5:1) was obtained from slower-eluted fractions (total yield 71.0 mg, 64% ;α:β = 5:1). T.l.c. of the former mixture with 3:1 toluene–ethyl acetate showed two spots, at R_F 0.31 (**4**) and 0.34 (**5**). Their ratios were determined from the intensity ratios of their H-5 signals in ^{1}H-n.m.r. spectra. Recrystallization of the latter mixture from chloroform–hexane gave colorless needles of **4** (48.9 mg, 44%), m.p. 108°, $[\alpha]_D^{25}$ +72° (*c* 1, chloroform); ν_{max}^{KBr} 1240 (C=O of Ac), 1640 (C=C), and 1745 cm^{-1} (C=O of Ac); n.m.r. see Tables I-III; m.s.: *m/z* 373 $[M + H]^+$, 331 $[M - allyl]^+$, 314 $[M - OAc + H]^+$, and 313 $[M - OAc]^+$.

Anal. Calc. for $C_{17}H_{24}O_9$: C, 54.83; H, 6.50. Found: C, 54,78; H,6.52.

For preparative purposes, the procedure could be scaled-up by use of 5.07 g (13.0 mmol) of **1** in acetonitrile (100 mL) with allyltrimethylsilane (20.6 mL, 130 mmol) and $BF_3{\cdot}Et_2O$ (16.1 mL, 130 mmol) in reaction for 12 h at 80° and extraction of the product into chloroform (150 mL). The resultant syrup (5.01 g) was eluted from a column (2.5 x 31 cm) of silica gel with 5:1 toluene–ethyl acetate to give 63% of **4** in admixture with some **5**; recrystallization from chloroform–hexane gave colorless needles of pure **4**; yield 2.18 g (45%).

*(b) From methyl tetra-*O*-acetyl-*α*-*D*-glucopyranoside* (**2**). To a solution of **2** (111 mg, 0.31 mmol) in dry acetonitrile (2.3 mL) was added allyltrimethylsilane (0.24 mL, 1.5 mmol) and $BF_3{\cdot}Et_2O$ (0.19 mL, 1.5 mmol). The mixture was heated for 24 h at 80° under N_2. The same amounts of allyltrimethylsilane and $BF_3{\cdot}Et_2O$ were again added, and the mixture was heated for a further 24 h. The same treatment as described in (*a*) gave a 5:1 mixture of **4** and **5** (25.7 mg, 23%).

*(c) From tetra-*O*-acetyl-*α*-*D*-glucopyranosyl bromide* (**3**). To a solution of **3**

(108 mg, 0.26 mmol) in dry acetonitrile (2 mL) was added allyltrimethylsilane (0.42 mL, 2.6 mmol) and $BF_3{\cdot}Et_2O$ (0.32 mL, 2.6 mmol). The mixture was heated at 80° under N_2. Further additions of allyltrimethylsilane (0.42 mL, 0.21 mL) and $BF_3{\cdot}Et_2O$ (0.32 mL, 0.16 mL) were required, one and two days after the reaction started, to consume all of the **3**. After the mixture had been heated for a total of 3 days, processing as described in (*a*) gave a 5:1 mixture of **4** and **5** (14.7 mg, 15%).

3-(α-D-Glucopyranosyl)-1-propene (**8**). —The tetraacetate **4** (1.48 g, 4.0 mmol) was treated with 0.04M methanolic sodium methoxide (20 mL) for 45 min at room temperature, and the solution was then made neutral with Amberlite IR-120 (H^+) resin. The resin was filtered off, washed with methanol, and the filtrate was evaporated to yield a crystalline, chromatographically homogeous solid (0.81g, 100%) that was recrystallized from 2-propanol with little loss to give the pure deacetylated product **8** as needles; m.p. 150–151° (lit.[14] m.p. 153–156°), $[\alpha]_D^{20}$ +94° (*c* 0.7, water).

Anal. Calc. for $C_9H_{16}O_5$: C, 52.93; H,7.90. Found: C, 52.97; H, 7.92.

3-(Tetra-O-acetyl-β-D-glucopyranosyl)-1-propene (**5**).–The procedure of Shulman *et al.*[8] was modified. A solution of the bromide **3** (526 mg, 1.3 mmol) in dry oxolane (5 mL) was added slowly during 2 h to a stirred mixture of M allylmagnesium bromide in ether (16 mL) and dry oxolane (16 mL) under N_2 in an oil bath maintained at 40°. The mixture was then heated for 5 h at 60° and subsequently cooled to room temperature. Water (3.5 mL) and 12M HCl (1.7 mL) were added, bringing the mixture to pH 1.The water layer was made neutral with $NaHCO_3$, washed with ether, and evaporated to a pale-yellow solid. The solid was dissolved in acetic anhydride (14 mL) at 100°, sodium acetate (530 mg, 6.5 mmol) was added, and the mixture was heated for 3 h at 100°. The cooled solution was evaporated to a syrup that was dissolved in chloroform (50 mL). The solution was successively washed with water, aqueous $NaHCO_3$, and water, dried (Na_2SO_4), and evaporated to give a dark syrup (643 mg) that was purified on a column of silica gel with 6:1 toluene–ethyl acetate and 3:1 hexane–ethyl acetate to give colorless crystals of **5** (118 mg, 25%), which were recrystallized from ether–petroleum ether; m.p. 77–78°, $[\alpha]_D^{25}$ – 6° (*c* 0.2, chloroform); lit.[8] m.p. 78–78.5°, $[\alpha]_D^{20}$ – 8° (*c* 1, chloroform); n.m.r. see Tables I–III; m.s.: *m/z* 373 $[M + H]^+$, 331 $[M - allyl]^+$, 314 $[M - OAc + H]^+$, and 313 $[M - OAc]^+$. The yield of **3** was only 5% when the published procedure[8] was employed.

5-(Tetra-O-acetyl-α- (**6**) *and -β-D-glucopyranosyl)-(E)-1,3-pentadiene.* (**7**). — To a solution of **1** (107 mg, 0.27 mmol) in dry acetonitrile (2 mL) were added (*E*)-penta-2,4-dienyltrimethylsilane (213 mg, 1.5 mmol) and $BF_3{\cdot}Et_2O$ (0.04 mL, 0.32 mmol). The mixture was heated overnight at 60° whereupon additional (*E*)-penta-2,4-dienyltrimethylsilane (118 mg, 0.84 mmol) and $BF_3{\cdot}Et_2O$ (0.04 mL) were added to the solution, and the mixture was heated for a further 6 h. The same processing as described for the preparation of **4** gave a thick syrup of a 4:1 mixture of **6** and **7** (35.7 mg, 33%), and crystals of unreacted **1** (18.0 mg, 17%) were recovered. No further purification was performed because the mixture of **6** and **7** readily

polymerized on being kept at room temperature. The n.m.r. parameters for the separate products **6** and **7** were readily extracted from the spectra of the mixture (see Tables I and II).

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