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Dimethyl-(4-methyl-1-cyclohexenyl)methyl and 2-(1-Methylethylidene)-5-methylcyclohexyl Ethers from Pulegone[1]

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DIMETHYL-(4-METHYL-1-CYCLOHEXENYL)METHYL AND 2-(1-METHYLETHYLIDENE)-5-METHYLCYCLOHEXYL ETHERS FROM PULEGONE[1]

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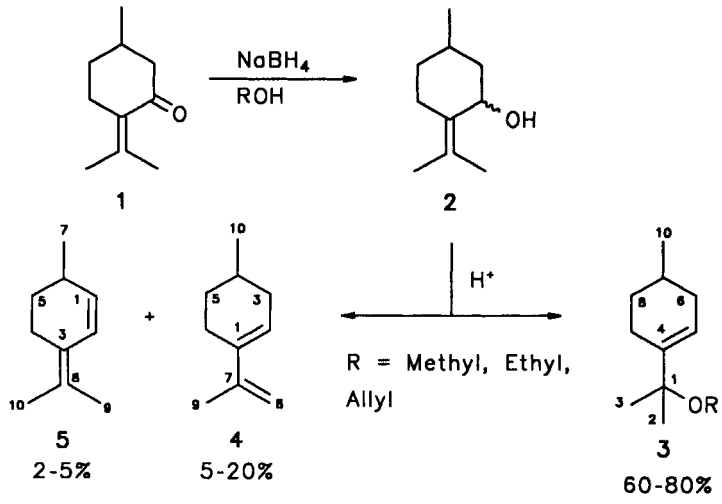
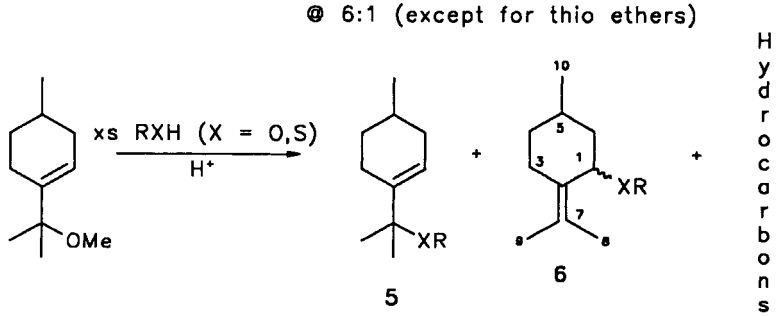
ABSTRACT $NaBH_4$ reduction of pulegone (**1**) in short chain alcohols followed by acidification of the reaction mixture gives dimethyl-(4-methyl-1-cyclohexenyl) ethers. Acid catalyzed transetherification of these ethers in longer chain alcohols yields mixtures of the title compounds.

Pulegone (**1**) is a bioactive terpene undergoing evaluation at this laboratory as a foundation for biorational herbicides[2]. In the course of reducing the ketone to prepare (**2**) for further structural modification, acidification of the reaction mixture produced an unexpected addition-elimination reaction leading to ethers as shown in scheme 1. The acidification step was understandably exothermic and two hydrocarbons[3,4] (**4** and **5**, Scheme 1) resulting from complete elimination were also formed in varying amounts. If acidification is carried out slowly with minimum temperature elevation, the yield of ether can be as high as 80% with limited amounts of the acompanying hydrocarbons being formed.

In addition to this preparation, longer-chain ethers can be produced by acid-catalyzed transetherification of **1**. Benzyl, 4-methoxybenzyl, salicyl, n-propyl, n-butyl, 3-methyl-2-butenyl, citronnelyl and geranyl ethers have been prepared and isolated as is shown in scheme 2. However, these species are accompanied by the isomeric 2-(1-



Scheme 1



Scheme 2

methylethylidene)-5-methylcyclohexyl ethers (**6**) that occur in about one-sixth of the amount of the major products (**3**).

The transetherification and isomerization (or addition/elimination) reactions are reversible and their extent depends on the concentrations of the ether(s) and alcohols

present. The speed of the reaction is dependent on the ether concentration as well as the structure of the alcohol. For example, n-propyl and n-butyl alcohols reach equilibrium in about 24 hours whereas reactions with the aromatic (benzyl, 4-methoxybenzyl and salicyl) alcohols were completed in about 90 minutes. Citronellol and geraniol took over 3 days to equilibrate.

Ethers from bifunctional alcohols (mercaptoethanol, ethyleneglycol monoacetate, 2-nitropropanol, 2-nitroethanol, acetol, 3-hydroxypropionitrile, methyl glycolate, cysteine ethyl ester and 1-(2-hydroxyethyl)pyrrolidine were also synthesized and isolated. Only the thio ether was formed from mercaptoethanol (execllent yield) and the ratio of isomers was nearly equal. Data from this compound and its acetate are given in the tables. Ethylene glycol did not react but its monoacetate gave good yields with the expected isomeric ratio. Hydrolysis of the ester then produced the hydroxy ether. The nitro compounds and 3-hydroxypropionitrile behaved similarly to the monofunctional alcohols. Methyl glycolate, cysteine ethyl ester and the hydroxyethyl pyrrolidine reacted poorly (@ 10 percent yield) and, as in the case of mercaptoethanol, the isomeric ratio in the cysteine ethyl ester preparation was about 1:1.

Proton and carbon NMR spectra of the ethers and hydrocarbons plus salient features of their mass spectra are summarized in Tables 1 - 3. These ethers (previously unknown compounds) are undergoing evaluation for activity in a variety of bioassay systems.

EXPERIMENTAL

Solvents were ACS grade and all reactants were purchased from Aldrich Chemical Co., Milwaukee, WI.

Reduction of pulegone. Fifty grams of $NaBH_4$ were gradually added (under stirring) to 100g of pulegone in 300 mL of MeOH (or EtOH or allyl alcohol) in an ice bath. The solution was allowed to come to room temperature and stirring was continued overnight.

Table 1. ^{1}H- and ^{13}C-NMR Chemical Shifts and Prominent Diagnostic Mass Spectral Ions for Ethers of Structure 3

	R GROUP					
Carbon no.	CH_3-O	CH_3-CH_2-O	CH_3-$(CH_2)_2$-O	CH_3-$(CH_2)_3$-O	$(CH_3)_2$-C=CH-CH_2-O	CH_2=CH-CH_2-O
				PROTON		
2,3	1.04 s, 1.06 s	1.18 s, 1.19 s	1.24 s, 1.25 s	1.21 s, 1.22 s	1.25 s, 1.26 s	1.26 s, 1.27 s
5	5.39 dd (J=2.2, 2.5)	5.49 dd (J=2.0, 2.2)	5.56 dd (J=2.2, 2.1)	5.55 br s	5.57 br s	5.88 dd (J=2.2, 1.8)
6,7,8,9	1.4 - 1.9 m	1.5 - 2.0 m	1.3 - 2.0 m	1.3 - 2.0 m	1.3 - 2..4m	1.3 - 2.1 m
10	0.76 d (J=6.3)	0.87 d (J=6.2)	0.87 d (J=6.3)	0.92 d (J=6.1)	0.92 d (J=6.2)	0.93 d (J=6.3)
Other	2.81 s CH_3O	1.05 t (J=7.1) CH_3 3.12 m CH_2O	0.97 t (J=7.5) CH_3 1.69 m CH_2 3.06 m CH_2O	0.90 t (J=7.2) CH_3 1.42 - 1.47 m CH_2 3.05 m CH_2O	1.60 s, 1.68 s CH_3 3.62 m CH_2O 5.26 t (J=7.0) =CH	3.67 m CH_2O 5.06 dd (J=10.4,1.7) =CH_2 5.21 dd (J=17.2,1.7) =CH_2 5.85 ddd(J=17.2,10.4,1.7) =CH
				CARBON		
1	76.3	76.4	76.4	76.3	77.4	77.3
2,3,10	21.3, 24.1, 25.6	21.6, 25.0, 26.3	21.8, 25.1, 26.4	21.7, 25.0, 26.4	21.7, 25.1, 26.5	21.7,25.1,26.3
4	139.8	140.7	141.9	140.8	140.5	140.4
5	121.9	121.6	121.7	121.7	122.3	122.3
6,8,9	23.3, 31.0, 33.7	23.6, 31.2, 33.8	23.6, 31.3, 34.0	23.7, 31.3, 33.9	23.6, 31.2, 33.9	23.6,31.2,33.9
7	28.1	28.3	26.8	28.4	28.3	28.3
Other	49.4 CH_3O	15.8 CH_3 57.2 CH_2O	10.4 CH_3 23.7 CH_2 63.5 CH_2O	14.0 CH_3 19.5, 32.7 CH_2 61.7 CH_2O	17.8, 25.8 CH_3 59.0 CH_2O 122.0 =CH 135.0 =C	63.6 CH_2O 115.5 =CH_2 136.0 =CH
				MASS SPECTRUM		
	168(5),153(100), 121(40),73(50), 43(60)	182(3),167(95), 139(25),121(25), 43(100)	196(5),181(70), 139(95),43(100)	210(5),195(55), 139(95),43(100)	207(3),138(45),95(65) 69(60),41(100)	179(15),138(20),95(35) 43(100)

Table 1 (cont.)

Carbon no.	R GROUP: $(CH_3)_2$-C=CH-$(CH_2)_2$-CH(CH_3)-$(CH_2)_2$-O	R GROUP: $(CH_3)_2$-C=CH-$(CH_2)_2$-C(CH_3)=CH-CH_2-O	R GROUP: ϕ-CH_2-O	R GROUP: *p*-OCH_3-ϕ-CH_2-O	R GROUP: *o*-OH-ϕ-CH_2-O
			PROTON		
2,3	1.23 s, 1.24 s	1.27 s 1.29 s	1.24 s, 1.25 s	1.37 s, 1.39 s	1.40 s, 1.42 s
5	5.75 dd (J=2.2, 2.5)	5.60 dd (J=2.0, 2.6)	5.83 dd (J=2.2, 2.4)	5.71 br s	5.75 br s
6,7,8,9	1.2 - 2.1 m	1.2 - 2.0 m	1.8 - 2.8 m	1.2 - 3.8 m	1.7 - 2.2 m
10	0.93 d (J=6.3)	0.94 d (J=7.2)	1.12 d (J=6.2)	0.99 d (J=6.1)	0.99 d (J=6.3)
Other	0.84 d (J=6.2) CH_3 1.2 - 2.1 m CH, CH_2 1.58 s, 1.67 s CH_3 3.11 m CH_2O 5.02 m =CH	1.58 s, 1.61 s, 1.67 s CH_3 1.0 - 2.0 m CH_2 3.67 m CH_2S 5.08 m, 5.28 m =CH	4.13 d (J=11.5) CH_2O 4.21 d (J=11.5) CH_2O 7.4 - 7.5 aromatic	3.79 s CH_3O 4.17 d (J=10.8) CH_2O 4.36 d (J=10.8) CH_2O 6.9 - 7.2 aromatic	4.44 d (J=12.1) CH_2O 4.51 d (J=12.1) CH_2O 6.2 - 7.2 aromatic 8.3 OH
			CARBON		
1	76.4	76.5	77.0	77.1	80.0
2,3,10	21.8, 23.8, 25.8	21.8, 25.2, 26.5	21.6, 23.8, 26.3	21.7, 25.1, 26.5	21.6 23.8, 26.0
4	140.8	140.6	140.2	140.3	138.8
5	121.7	122.1	122.2	122.3	123.7
6,8,9	23.8, 31.3, 34.0	23.7, 31.3, 39.7	23.7.31.3,33.8	23.8, 31.2, 34.0	23.8, 31.1, 33.9
7	28.4	28.4	28.2	28.4	28.1
Other	17.6, 19.6, 25.0 CH_3 25.4, 37.3, 37.6 CH_2 29.7 CH 60.4 CH_2O 121.7 =CH 130.9 =C	23.7, 25.7, 28.4 CH_3 26.4, 34.2 CH_2 59.2 CH_2O 122.2, 124.1 =CH 124.4, 138.1 =C	64.3 CH_2O 126.7 - 139.6 aromatic	55.1 CH_3O 64.1 CH_2O 113.6 - 158.7 aromatic	64.7 CH_2O 116.4 - 128.5 aromatic 156.3 aromatic COH
			MASS SPECTRUM		
	277(3),193(5),137(100), 81(30)	275(2),153(10),137(80) 95(95),81,100)	244(2),229(4),153(45) 138(55),91(100)	274(3),138(85), 121(100),95(40)	260(2),137(100),107(45), 95(80),81(70),43(50)

(continued)

Table 1. (cont.)

Carbon no.	R GROUP: $HO-CH_2-CH_2-S$	$Ac-O-CH_2-CH_2-S$	$HO-CH_2-CH_2-O$	$Ac-O-CH_2-CH_2-O$	$CH_3-CH(NO_2)-CH_2-O$	$O_2N-CH_2-CH_2-O$
				PROTON		
2,3	1.28 s, 1.35 s	1.29 s, 1.36 s	1.05 s, 1.06 s	1.18 s, 1.19 s	1.19 s, 1.20 s	1.18 s, 1.20 s
5	5.48 br s	5.50 br s	5.38 br s	5.52 br s	5.57 br s	5.57 br s
6,7,8,9	1.2 - 2.4 m	1.2 - 2.4 m	1.3 - 2.2 m	1.3 - 2.2 m	1.3 - 2.2 m	1.2 - 2.0 m
10	0.88 d (J=6.3)	0.90 d (J=6.3)	0.72 d (J=6.2)	0.86 d (J=6.3)	0.91 d (J=6.4)	0.88 d (J=6.4)
Other	2.44 m CH_2S	2.00 s CH_3	3.00 m CH_2O	1.97 s CH_3	1.44 d (J=6.8) CH_3	3.60 m CH_2O
	3.55 t (J=6.4) CH_2O	2.44 m CH_2O	3.41 m CH_2O	3.25 m CH_2O	3.56 m CH_2O	4.38 t (J=5.0) CH_2NO_2
		4.04 t (J=7.1) CH_2O		4.05 m CH_2O	4.61 m $CH(NO_2)$	
				CARBON		
1	49.6	49.8	76.4	77.0	77.3	77.3
2,3,10	21.3, 27.8, 28.2	20.8, 27.7, 27.8	21.2, 23.1, 25.7	21.5, 24.7, 26.1	21.6, 24.3, 25.8	21.6, 23.4, 25.8
4	139.8	139.8	139.6	139.8	139.4	139.1
5	121.8	122.0	121.8	122.4	122.8	122.9
6,8,9	24.4, 31.3, 34.0	24.4, 31.4, 34.0	23.2, 30.7, 33.4	23.4, 31.0, 33.8	23.5, 31.0, 33.8	24.2, 30.9, 33.7
7	28.2	28.2	27.8	28.2	28.2	28.1
Other	32.5 CH_2S	20.8 CH_3 37.8 CH_2S	61.4 CH_2O	20.8 CH_3	15.8 CH_3 64.0 CH_2O	58.3 CH_2O
	61.3 CH_2O	63.9 CH_2O 170.6 C=O	63.1 CH_2O	60.3, 64.1 CH_2O	83.0 $CH(NO_2)$	75.8 CH_2NO_2
				170.8 C=O		
				MASS SPECTRUM		
	214(2),137(100), 95(75),81(70)	256(3),196(2), 137(100),95(70),81(60)	198(2),183(15), 139(15),136(20), 81(25),43(100)	225(2),136(25), 121(8),87(100),43(75)	241(2),226(10),137(35), 95(45),88(40),43(70), 41(100)	227(2),212(35),167(5) 139(25),121(20),95(25), 74(95),42(100)

Table 1 (cont.)

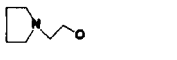
Carbon no.	CH_3-CO-CH_2-O	NC-CH_2-CH_2-O	CH_3-CO_2-CH_2-O	C_2H_5-CO_2-CH(NH_2)-CH_2-S	
				PROTON	
2,3	1.09 s, 1.10 s	1.24 s, 1.25 s	1.19 s, 1.19 s	1.23 s, 1.30 s	1.04 s, 1.05 s
5	5.43 br s	5.59 br s	5.53 br s	5.45 br s	5.45 br s
6,7,8,9	1.3 - 2.2 m	1.3 - 2.2 m	1.3 - 2.1 m	1.3 - 2.2 m	1.3 - 2.1 m
10	0.74 d (J=6.4)	0.91 d (J=6.2)	0.83 d (J=6.2)	0.83 d (J=6.5)	0.75 d (J=6.5)
Other	1.95 s CH_3	2.47 m CH_2	3.60 s CH_3	1.16 t (J=7.1) CH_3	1.3 - 2.1 m CH_2
	3.53 m CH_2O	3.32 m CH_2O	3.71 d (J=6.4) CH_2O	2.37 dd (J=7.6,7.7) CH_2S	2.14 t (J=7.2) CH_2N
				2.53 dd (J=7.6,7.7) CH_2S	3.10 m CH_2N 3.40 m CH_2N
				3.43 m CH(NH_2)	3.35 t (J=7.0) CH_2O
				4.07 t (J=7.1) CH_2O	
				CARBON	
1	77.4	77.6	78.2	49.6	76.5
2,3,10	21.2, 25.6, 26.0	21.6, 24.6, 26.0	21.4, 24.5, 25.8	21.4, 24.2, 27.5	21.3, 24.5, 25.9
4	138.9	134.9	139.0	139.5	139.5
5	122.9	122.9	123.2	121.9	123.0
6,8,9	23.3, 30.7, 33.4	23.6, 31.0, 33.7	23.4, 30.8, 33.7	27.6, 31.2, 33.8	23.2, 30.8, 33.5
7	27.8	28.2	28.0	28.0	27.9
Other	24.3 CH_3	19.3 CH_2CN	51.4 CH_3	13.9 CH_3 34.4 CH_2S	17.8 CH_2 19.3 CH_2
	68.5 CH_2O	57.3 CH_2O	60.8 CH_2O	54.2 CH(NH_2)	30.5 CH_2N 43.1 CH_2N
	208.6 C=O	118.1 CN	171.2 C=O	60.8 CH_2O 173.9 C=O	48.8 CH_2N 60.4 CH_2O
				MASS SPECTRUM	
	195(3),165(2), 137(90),121(90), 107(20),91(85), 43(100)	207(10),192(40) 149(5),136(20), 121(55),43(100)	211(5),136(70),121(100), 107(65),93(90),79(50), 43(85)	285(10),212(5),150(25) 137(100),95(80),81(75) 98(40),79(30),41(85)	192(5),137(20),130(100), 127(25),121(20),112(35),

Table 2. ^{1}H- and ^{13}C-NMR Chemical Shifts and Prominent Diagnostic Mass Spectral Ions for Ethers of Structure 6.

Carbon no.	R Group: CH_3-$(CH_2)_2$-O	CH_3-$(CH_2)_3$-O	$(CH_3)_2$-C=CH-CH_2-O	$(CH_3)_2$-C=CH-$(CH_2)_2$-CH(CH_3)-$(CH_2)_2$-O	$(CH_3)_2$-C=CH-$(CH_2)_2$-C(CH_3)=CH-CH_2-O
			PROTON		
1	4.37 br s	4.36 br s	4.41 br s	4.35 br s	4.42 br s
3,4,5,6	1.3 - 2.4 m	1.3 - 2.4 m	1.3 - 2.4 m	1.3 - 2.4 m	1.6 - 2.4 m
7	0.82 d (J=6.4)	0.82 d (J=6.4)	0.82 d (J=6.4)	0.82 d (J=6.4)	0.82 d (J=6.5)
9,10	1.70 s, 1.71 s	1.69 s, 1.71 s	1.70 s, 1.71s	1.70 s, 1.71 s	1.70 s, 1.71 s
Other	0.89 t (J=7.4) CH_3	0.89 t (J=7.3) CH_3	1.62 s, 1.69 s CH_3	0.87 d (J=6.4) CH_3	1.59 s, 1.61 s, 1.67 s CH_3
	1.54 m CH_2	1.3 - 2.4 m CH_2	3.75 m CH_2O	1.67 s, 1.69 s CH_3	1.6 - 2.4 m CH_2
	3.16 t (J=6.7) CH_2O	3.21 m CH_2O	5.75 m =CH	1.3 - 2.4 m CH, CH_2	3.79 m CH_2O
				3.64 m CH_2 5.33 m =CH	5.08 m, 5.33 m =CH
			CARBON		
1	73.3	73.3	76.5	73.4	72.9
2,8	121.7, 131.3	125.3, 131.3	122.2, 135.0	130.9, 131.4	131.5, 138.8
3,4,6	25.0, 36.0, 41.3	25.1, 36.0, 41.3	25.0, 31.0, 33.9	25.5, 36.1, 41.4	25.6, 36.0, 41.3
5	26.7	26.8	26.4	26.8	26.8
7,9,10	19.9, 20.3, 26.8	19.9, 20.4, 22.2	21.7, 23.6, 25.8	19.9, 20.4, 22.2	19.9, 20.4, 22.3
Other	10.8 CH_3	14.0 CH_3	17.8, 28.3 CH_3	17.6, 19.9, 26.7 CH_3	22.1, 26.8, 32.2 CH_3
	22.2 CH_2	19.6, 32.2 CH_2	59.0 CH_2O	25.1, 30.3, 36.9, 37.1 CH_2	25.7 , 37.8 CH_2
	68.4 CH_2O	66.5 CH_2O	122.0 =CH	29.6 CH 65.0 CH_2O	63.4 CH_2O
			135.5 =C	124.9 =CH 140.5 =C$(CH_3)_2$	122.1, 124.1 =CH
					126.7, 131.2 =C
			MASS SPECTRUM		
	196(35),181(55),	210(15),195(25)	222(3),207(7),138(20),	277(5),193(5),153(10),	275(7),229(3),173(5)
	139(75),41(100)	139(55),41(100)	95(40),81(50),69(70),	137(100),81(30)	137(100),95(70),81(80)

Table 2 (cont.)

Carbon no.	ϕ-CH_2-O	*p*-OCH_3-ϕ-CH_2-O	R GROUP: *o*-OH-ϕ-CH_2-O	HO-CH_2-CH_2-S	Ac-O-CH_2-CH_2-S
			PROTON		
1	4.48 br s	4.45 br s	4.56 br s	4.12 br s	4.19 br s
3,4,5,6	1.3 - 2.4 m	1.3 - 2.4 m	1.3 - 2.4 m	1.3 - 2.5 m	1.3 - 2.5
7	0.85 d (J=6.5)	0.83 d (J=6.5)	0.86 d (J=6.4)	0.77 d (J=6.2)	0.81 d (J=6.6)
9,10	1.66 s, 1.72 s	1.66 s, 1.71 s	1.66 s, 1.67 s	1.63 s, 1.64 s	1.68 s, 1.69 s
Other	4.24 d (J=12.0) CH_2O	3.78 s OCH_3	4.42 d (J=12.6) CH_2O	2.51 t (J=6.2) CH_2S	2.02 s CH_3
	4.43 d (J=12.0) CH_2O	4.29 d (J=11.6) CH_2O	4.68 d (J=12.6) CH_2O	3.58 t (J=6.2) CH_2O	2.56 t (J=7.0) CH_2S
	7.3 - 7.5 aromatic	4.41 d (J=11.6) CH_2O	6.8 - 7.2 aromatic		3.21 m CH_2O
		6.8 - 7.2 aromatic	8.23 OH		
			CARBON		
1	73.0		73.9	43.4	44.0
2,8	126.2, 130.7		124.7, 128.2	124.5, 130.5	124.9, 130.6
3,4,6	25.2, 36.0, 41.3		25.1, 35.6, 41.0	27.1, 33.8, 40.8	24.6, 130.6, 40.6
5	26.9		26.9	27.0	27.2
7,9,10	119.9, 20.4, 22.2		20.0, 20.5, 22.1	20.2, 20.4, 21.9	20.3, 20.5, 22.0
Other	68.5 CH_2O		68.6 CH_2O	35.8 CH_2S	20.9 CH_3 35.9 CH_2S
	126.7 - 128.9 aromatic		116.4 - 129.0 aromatic	60.8 CH_2O	63.8 CH_2O 170.8 C=O
			156.6 =COH		
			MASS SPECTRUM		
	229(3),138(45),	274(5),137(15),	260(2),218(7),161(3),	214(3),169(1),137(100),	256(5),196(2),137(100)
	95(20),91(100)	121(100),95(10)	107(80),78(100)	95(80),81(70)	95(80),81(35),43(25)

(continued)

Table 2. (cont.)

Carbon no.	HO-CH_2-CH_2-O	Ac-O-CH_2-CH_2-O	CH_3-$CH(NO_2)$-CH_2-O	O_2N-CH_2-CH_2-O	CH_3-CO-CH_2-O
			R GROUP		
			PROTON		
1	4.39 br s	4.42 br s	4.67 br s	4.45 br s	4.44 br s
3,4,5,6	1.3 - 2.4 m	1.3 - 2.4 m	1.3 - 2.4 m	1.3 - 2.4 m	1.6 - 2.4 m
7	0.89 d (J=6.4)	0.82 d (J=6.2)	0.80 d (J=6.6)	0.79 d (J=6.5)	0.84 d(J=6.5)
9,10	1.65 s, 1.67 s	1.70 s, 1.71 s	1.69 s, 1.71 s	1.69 s, 1.71 s	1.65 s, 1.68 s
Other	3.31 m CH_2O	2.05 s CH_3	1.48 d (J=6.9) CH_3	3.75 dd (J=3.8,10.0) CH_2O	2.13 s CH_3
	3.62 m CH_2O	3.44 m CH_2O	3.47 dd (J=4.3,10.2) CH_2O	4.43 dd (J=3.8,10.0) CH_2O	3.81 m CH_2O
		4.55 m CH_2O	3.62 dd (J=4.3,10.2) CH_2O	4.49 m CH_2NO_2	
			4.69 m $CH(NO_2)$		
			CARBON		
1	73.8	73.8	74.5	73.9	73.9
2,8	126.0, 130.4	126.3, 130.5	126.7, 130.1	124.7, 128.2	127.5, 129.5
3,4,6	25.0, 35.7, 41.0	24.9, 35.9, 41.1	25.0, 35.6, 40.9	25.1, 35.6, 41.0	25.0, 37.5, 41.0
5	26.6	26.7	26.5	26.9	26.4
7,9,10	19.8, 20.3, 22.1	19.9, 20.4, 22.1	19.9, 20.3, 22.0	20.0, 20.5, 22.1	19.9, 20.4, 22.1
Other	61.9 CH_2O	21.0 CH_3	15.8 CH_3 68.2 CH_2O	68.6 CH_2O	27.7 CH_3
	67.8 CH_2O	64.0, 64.4 CH_2O	82.2 $CH(NO_2)$	75.5 CH_2NO_2	72.5 CH_2O
		171.1 C=O			208.6 C=O
			MASS SPECTRUM		
	136(5),121(4), 107(5),95(5), 87(100),43 (90)	153(5),136(15),121(10) 107(7),87(100),43(55)	226(10,198(3),137(15), 121(10),95(30),81(40), 41(100)	227(4),212(15),184(3), 167(5),139(15),121(10), 74(40),41(100)	195(2),153(5),137(10) 121(5),95(50),67(20), 67(20),43(100)

Table 2 (cont.)

Carbon no.	$NC-CH_2-CH_2-O$	$CH_3-O_2C-CH_2-O$	$C_2H_6-O_2C-CH(NH_2)-CH_2-O$	
			PROTON	
1	4.44 br s	4.54 br s	4.12 br s	4.34 br s
3,4,5,6	1.2 - 2.4 m	1.6 - 2.4 m	1.2 - 2.4 m	1.6 - 2.4 m
7	0.83 d (J=6.3)	0.89 d(J=6.6)	0.77 d (J=6.5)	0.81 d (J=6.5)
9,10	1.70 s, 1.71 s	1.65 s, 1.68 s	1.64 s, 1.65 s	1.65 s, 1.68 s
Other	2.54 t (J=6.5) CH_2CN	3.70 s CH_3	1.20 t (J=7.1) CH_3	1.6 - 2.4 CH_2
	3.45 m CH_2O	3.84 d (J=4.8) CH_2O	2.46 dd (J=4.2,8.1) CH_2S	2.34 m CH_2N 3.40 m CH_2N
			2.70 dd (J=4.2,8.1) CH_2S	3.50 m CH_2N 3.52 m CH_2O
			3.50 m $CH(NH_2)$ 4.13 m CH_2O	
			CARBON	
1	74.3	73.8	43.6	73.8
2,8	126.8, 130.1	127.8, 129.5	125.0, 130.2	126.2, 130.3
3,4,6	24.7, 31.7, 41.3	25.0, 35.7, 40.9	24.4, 31.8, 40.4	25.0, 35.8, 41.2
5	26.7	26.5	27.1	26.8
7,9,10	19.9, 20.5, 22.1	19.8, 20.4, 22.0	20.2, 20.5, 22.0	19.9, 20.4, 22.2
Other	19.1 CH_2CN	51.6 CH_3	14.0 CH_3 35.9 CH_2S	18.2 CH_2 19.0 CH_2
	61.5 CH_2O	64.0 CH_2O	54.2 $CH(NH_2)$	31.0 CH_2N 34.0 CH_2N
	118.2 CN	171.7 C=O	60.9 CH_2O 173.9 C=O	49.0 CH_2N 65.5 CH_2O
			MASS SPECTRUM	
	207(5),192(7),136(20), 121(55),93(30),81(20),	226(3),211(10),183(5), 136(50),121(100),93(75), 43(100)	285(2),212(2),150(20), 137(100),95(80),81(75),41(50) 43(90)	153(2),137(5),130(15), 121(10),112(20),(25), 93(20),79(43),41(100)

Table 3. ^{1}H- and ^{13}C-NMR Chemical Shifts and Prominent Diagnostic Mass Spectral Ions for Hydrocarbons 4 and 5.

Carbon No.	Diene 4	Literature[1]	Carbon no.	Diene 5	Literature[2]
			PROTON		
2	5.85 br s	5.8 br s	1	6.38 dd (J=10.1,2.3)	6.45 dd (J=10,2)
3,4,5,6	1.3 - 2.4 m	1.08 - 2.72 m	2	5.54 dm (J=10.1)	5.60 dm (J=10)
8	4.8 s, 5.0 s	4.72 s	4,5,6	1.5 - 2.4 m	
9	1.90 s	1.84 s	7	0.99 t (J=7.1)	1.09 t (J=7)
10	0.97 d (J=6.4)	0.96 d (J=5)	9,10	1.72s 1.79 s	1.80 s
			CARBON		
1,7	136.2, 143.5		1,2	124.7, 133.3	
2	124.4		3,8	126.1, 127.4	
3,5,6	25.9, 31.2, 34.5		4,5	25.5, 31.5	
4	28.2		6	30.4	
8	109.5		7,9,10	19.6,20.5,21.4	
9,10	20.6, 21.7				
			MASS SPECTRUM		
	136(50),121(100),93(90),107(10), 105(10),79(30)			136(40),121(35),107(50),93(60),79(100)	

[1]Ferro, A. and Naves, Y.-R. Helv. Chim. Acta 1974, 57, 1141. In CCl_4.
[2]Silvestri, M.G. J. Org. Chem 1983, 48, 2419. In CCl_4.

The bath was recharged with ice and 6N HCl was slowly added until the reaction mixture was acidic to pH paper. A good deal of frothing and foaming took place during addition of the acid so small amounts of ice were dropped directly into the reaction to help minimize the temperature. After the mixture had cooled to room temperature, it was extracted three times with 200 mL portions of Et_2O. The combined extracts were washed to neutral pH with water and concentrated by evaporation.

Preparation of ethers from 3. Samples of **3** (10 - 50g) and the appropriate mono- or bifunctional alcohol in five- to tenfold excess were stirred with a few drops of 6N HCl. Progress of the reaction was monitored by GC. When the concentration of **3** had reached a minimum (≤5% of the total peak areas) the reaction was terminated by the addition of water and the products were recovered by ether extraction as above.

Purification of products. All of the products were initially concentrated on silica columns (70 - 200 mesh, Aldrich) with hexane and/or mixtures of hexane and EtOAc as the eluting solvents. Progress of the chromatography was monitored by GC. Final purification of isomers was carried out by HPLC on C_{18} reverse-phase columns (M-9 ODS-2, Whatman) eluted with mixtures of water and acetone or on conventional phase silica columns (M-9 Partisil, Whatman) with hexane/EtOAc solutions.

Analytical Procedures. A Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a 15m DB-1 (J&W Scientific, Folsom, CA) column was temperature programmed from 100 to 200°C at 5°/min. Peak elution times and areas were determined by an SP4290 (Spectra Physics Inc., San Jose, CA) integrator. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ by a Brucker WM-300 spectrometer. Mass spectra were produced by a Hewlitt-Packard 5970 Mass Selective Detector.

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1. The mention of firm names or trade products does not imply that they are endorsed by the U. S. Department of Agriculture over other firms or similar products not mentioned.
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