

prepared from its bisulfite adduct,¹¹ distilled, and purified further by preparative GC (4 ft × 1/4 in. 10% SE 52 in series with 8 ft × 1/4 in. 20% DEGS on Chromosorb P). Preparation of all other reagents was as previously described.³ Base-catalyzed reaction conditions were used to minimize thioketal formation, and sample preparation for ¹³C NMR was similar to that for ¹H NMR.³ Typically, an aliquot of neat 3-MPA (0.04 mL, 4.6 mmol) was added to a 10-mm NMR tube containing anhydrous K₂CO₃ (13 mg, 90 μmol). After bubbling subsided, dioxane (0.9 mL) and cyclobutanone (0.2 mL, 2.7 mmol) were added. A 5-mm reference tube containing D₂O for the NMR field lock was held coaxially in the NMR tube by a Teflon-brand sleeve.

NMR Spectra. ¹H NMR spectra were recorded on an EM 390 90-MHz CW spectrometer or a 360-MHz Ft spectrometer interfaced to a Nicolet computer. Pulse widths were routinely 5 μs (90°), acquisition times were 4 s, and delay times were 1 s. Redfield 2-1-4 and soft pulse sequences were used in a few cases where small signals were measured in the presence of large ones.¹² For the pulse lengths used, the effective field of the carrier pulse decreases significantly after a few hundred hertz. By placing the carrier frequency midway between two signals to be measured, the difference in the effective field of the two signals was minimized. Measurements were made as soon as the addition reaction came to equilibrium. Routine conditions were used for acquiring ¹³C spectra (20° flip angle, 0.6 s acquisition time, and 1 s delay time).

Registry No. D₂O, 7789-20-0; 3-MPA-*d*₂, 95193-08-1; cyclobutanone, 1191-95-3; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8; tetrahydropyran-4-one, 29943-42-8; 4-piperidone, 41661-47-6.

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Gallium Trichloride and Superacid-Catalyzed Isomerization of Mixed Hexaalkylbenzenes and NMR Spectroscopic Study of the Intermediate Hexaalkylbenzenium Ions and Related Hexa- and Heptaalkylbenzenium Ions¹

George A. Olah,* Khosrow Laali, George Adler, Robert J. Spear, Richard Schlosberg, and Judith A. Olah

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089, and Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received August 21, 1984

A substantial number of methyl-substituted benzenium ions ranging from methylbenzenium ion to heptamethylbenzenium ion have been prepared and studied.² The charge distribution patterns in these ions have been discussed on the basis of their ¹H and ¹³C NMR data.²⁻⁴ Both the X-ray structure⁵ and CPMAS ¹³C NMR^{6,7} spectrum

(1) Considered as Friedel-Crafts Isomerization, Part 17, and Stable Carbocations, Part 260. For part 16, see: Olah, G. A.; Lin, C. H. *J. Am. Chem. Soc.* 1968, 90 6468. Part 259, see: Prakash, G. K. S.; Krishnamurthy, V. V.; Olah, G. A.; Farnum, D. G. *J. Am. Chem. Soc.*, in press.

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Table I. GaCl₃-Catalyzed Isomerization of Hexaalkylbenzenes in Freon-113 Solution at 30 °C^a

hexaalkylbenzene	isomer distribution (%)		
	ortho	meta	para
<i>o</i> -(C ₂ H ₅) ₂ (CH ₃) ₄ C ₆ (1)	32.4	40.5	27.1
<i>m</i> -(C ₂ H ₅) ₂ (CH ₃) ₄ C ₆ (2)	35.5	41.0	23.5
<i>p</i> -(C ₂ H ₅) ₂ (CH ₃) ₄ C ₆ (3)	37.6	44.6	17.8
<i>o</i> -(CH ₂ C(CH ₃) ₃) ₂ (CH ₃) ₄ C ₆ (4)	41.5	31.8	26.7
<i>m</i> -(CH ₂ C(CH ₃) ₃) ₂ (CH ₃) ₄ C ₆ (5)	31.4	34.2	34.4
<i>p</i> -(CH ₂ C(CH ₃) ₃) ₂ (CH ₃) ₄ C ₆ (6)	21.8	29.2	49.0

^a Average reaction time was 16 hs.

of isolated crystalline heptamethylbenzenium tetrachloroaluminate were reported. Ethyl-substituted benzenium ions including the heptaethylbenzenium ion were also reported. The heptaethylbenzenium ion was identified in the "red-oil" complex layers which are formed during the AlCl₃-catalyzed ethylation of benzene with ethylene.⁸

We now report the Friedel-Crafts isomerization of a series of mixed hexaalkylbenzenes, namely, isomeric diethyltetramethylbenzenes and dineopentyltetramethylbenzenes. We also studied their intermediate protonated hexaalkylbenzenium ions in FSO₃H-SbF₅ (4:1)/SO₂ and HF-SbF₅ (1:1)/SO₂ClF solution at -20 to -70 °C. Protonation of hexaisopropylbenzene in FSO₃H-SbF₅ (1:1)/SO₂ClF has also been carried out. Further we have also generated and studied by ¹³C NMR spectroscopy a series of related heptaalkylbenzenium ions formed by low-temperature ipso alkylation of hexamethyl- and hexaethylbenzene with Me₂C⁺H and Me₃C⁺ generated in SbF₅/SO₂ClF solution.

Results and Discussion

When hexaethylbenzene was treated with AlCl₃ in benzene solvent at 30 °C for 1 h no dealkylation or transalkylation was observed. Similarly treatment of isomeric diethyltetramethylbenzenes 1-3 with SbF₅ in 1,1,2-trifluoroethane (Freon-113) solution at 30 °C overnight gave no evidence of isomerization.

Addition of a proton source to the Lewis acid, however, promotes isomerization. Thus in our studies of Friedel-Crafts isomerization of hexaalkylbenzenes 1-6 we have found that GaCl₃ in Freon-113 as solvent and in the presence of a trace of water to provide a proton source is an efficient isomerization catalyst. No byproduct could be detected in these reactions. The results obtained are summarized in Table I.

When same isomeric 1-6 were dissolved in FSO₃H-SbF₅ (4:1)/SO₂ solution at -20 °C the ¹H NMR spectra of the resulting benzenium ions in all cases indicated formation and ready interchange of both possible, energetically similar, benzenium ions resulting from protonation ipso to methyl as well as ethyl groups. For example in case of 3

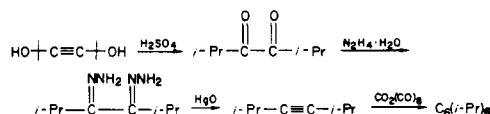
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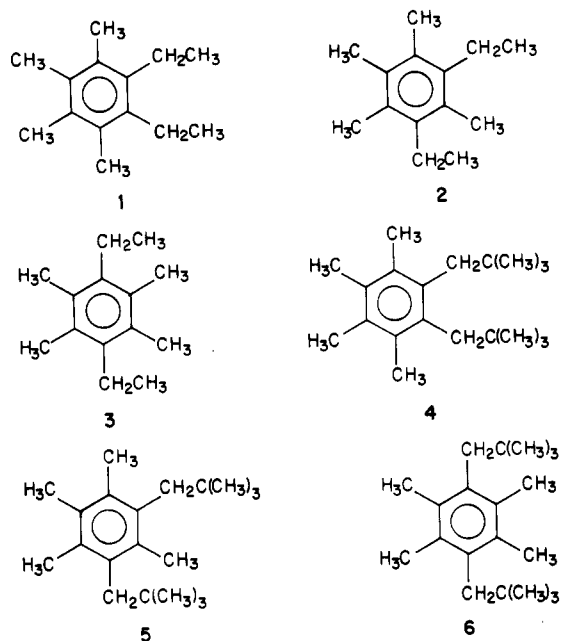
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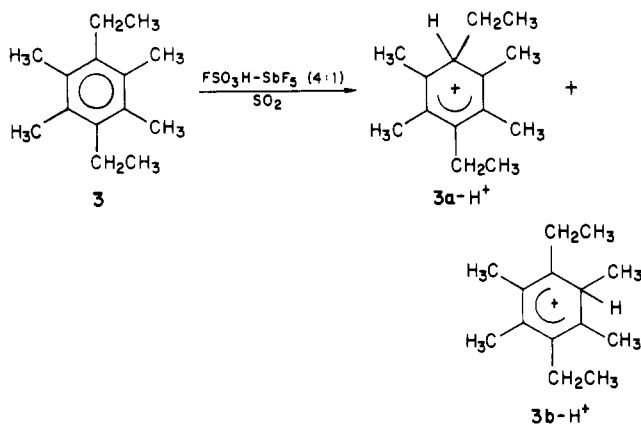
(9) Newman, M. S.; LeBlanc, J. R.; Karnes, H. A.; Axelrad, G. *J. Am. Chem. Soc.* 1963, 86, 868.

(10) This compound was synthesized in four steps starting from 2,5-dimethyl-3-hexyne-2,5-diol as follows:





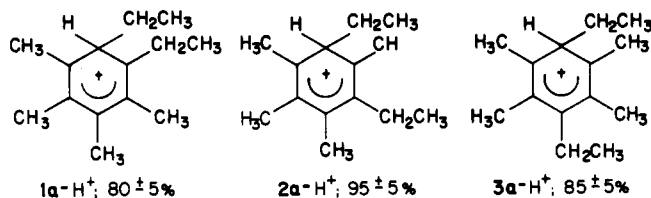
in going from the hydrocarbon to the arenium ion the ^1H NMR shows a $\Delta\delta$ of 0.89 ppm for the CH_2 group, 0.47 ppm for the CH_3 of the ethyl groups, and 0.95 ppm for the ring methyls. This almost equal deshielding observed for the methyl and methylene groups can be interpreted by the approximately equal likelihood of protonation of any of the ring positions, which would lead to a benzenium ion mixture of about $1/3$ 3a-H^+ and $2/3$ as 3b-H^+ . The ^1H NMR data of the studied hexaalkylbenzenes and their corresponding benzenium ions are summarized in Table II.



Quenching of the benzenium ion solutions resulting from protonation of 1, 2, and 3 showed isomerization (25–30%), i.e., formation of all three possible isomers from any given substrate. No dealkylation or disproportionation was observed. The ^1H NMR spectra of the recovered hydrocarbon mixtures showed no aromatic hydrogens and GLC showed only three isomeric diethyltetramethylbenzene in each case. The isomerizations thus are intramolecular in nature, in accordance with the poor leaving group ability of CH_3^+ and C_2H_5^+ .

In order to obtain static (nonexchanging) benzenium ions, we protonated compounds 1–3 in even stronger superacid system HF-SbF_5 (1:1)/ SO_2ClF at lower temperatures (-75°C). On the basis of the ^1H NMR and ^{13}C NMR spectra of the resulting benzenium ions (Tables III and IV), protonation is found to occur preferentially at the position ipso to the ethyl group, as evidenced by the appearance of an intense upfield triplet at δ 0.4 in the ^1H

NMR spectrum and an upfield $\text{C}_1\text{-CH}_3$ absorption in the ^{13}C NMR spectrum ($\delta_{13\text{C}}$ 7–8) for the methyl group of the C_1 -ethyl, which is forced over the pentadienylic moiety, hence resonating at unusually high field due to anisotropic shielding. In contrast, protonation ipso to methyl gives a C_1 -methyl resonance at normal field. The percentages of the major benzenium ions were determined by comparing the appropriate integral ratios in the ^1H NMR spectra and are shown below.

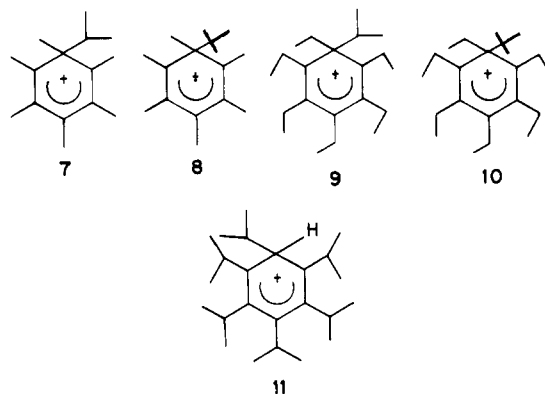


The ^1H NMR spectra also showed temperature dependence, characteristic of highly substituted benzenium ions. At -70°C broadening of the methyl and ethyl resonances commence, followed by (reversible) coalescence and eventual sharpening so that at -20°C only a single ethyl and one (3a-H^+) or two (1a-H^+ and 2a-H^+) methyl resonances were observed. In further experiments using the $\text{FSO}_3\text{H-SbF}_5(4:1)/\text{SO}_2\text{ClF}$ acid system, it was found that static benzenium ions can in fact be observed in this medium too at lower temperatures (-70°C). A similar temperature dependence of the ^1H NMR spectra was also observed.

The preference for protonation at the ethyl-bearing carbon is probably steric in origin, since the electronic differences between methyl and ethyl groups are small.

We also prepared and studied by ^{13}C NMR spectroscopy heptaalkylbenzenium ions by low-temperature alkylation of hexaalkylbenzenes with $\text{Me}_2\text{C}^+\text{H}$ and Me_3C^+ .

Slow addition of a cold solution of isopropyl cation generated from Me_2CHCl in $\text{SbF}_5/\text{SO}_2\text{ClF}$ to hexamethylbenzene in cold SO_2ClF with efficient mixing gave a homogeneous deep red solution. The ^{13}C NMR spectrum was consistent with the formation of isopropylhexamethylbenzenium ion (7) (Table V). Exchange broadening



of the methyl groups was also observed, suggesting that the ion was not completely frozen out. Raising the temperature led to decomposition and formation of side products. Similarly, addition of a cold solution of *tert*-butyl cation which was generated from *tert*-butyl chloride in $\text{SbF}_5/\text{SO}_2\text{ClF}$ solvent to hexamethylbenzene in SO_2ClF gave *tert*-butylhexamethylbenzenium ion 8. As previously shown for the heptaethylbenzenium ion,⁴ extensive positive charge is localized at positions ortho and para to the sp^3 -hybridized C_1 -carbon as evidenced by strong deshielding of C_2 , C_4 , and C_6 resonances relative to C_3 , C_5 (meta) where only moderate deshielding is observed as compared to the neutral precursor. Extending our studies,

Table II. ^1H NMR Data on Diethyltetramethyl- and Dineopentyltetramethylbenzenes and Their Corresponding Benzenium Ions in $\text{FSO}_2\text{H-SbF}_5(4:1)/\text{SO}_2$ at -20°C

substr	CH_2	ring CH_3	side chain	ring CH
1	2.61 (4 H) (q, $J = 7.6$ Hz)	2.02 (6 H) 2.09 (6 H)	1.03 (6 H) (t, $J = 7.6$ Hz)	
1-H ⁺	3.32 (q, $J = 7.5$ Hz)	3.02 (6 H) 3.08 (6 H)	1.27 (t, $J = 7.5$ Hz)	4.68
2	2.58 (4 H) (q, $J = 7.6$ Hz)	2.03 (6 H) 2.09 (6 H)	1.00 (6 H) (t, $J = 7.6$ Hz)	
2-H ⁺	3.17 (q, $J = 7$ Hz)	2.16 (3 H) 2.70 (3 H) 3.07 (9 H)	1.17 (t, $J = 7$ Hz)	4.63
3	2.58 (4 H) (q, $J = 7.25$ Hz)	2.03 (12 H)	0.95 (t, $J = 7.25$ Hz)	
3-H ⁺	3.47	2.98 (12 H)	1.42 (t, $J = 7$ Hz)	4.80
4	2.86 (2 H) 2.98 (2 H)	2.03 (6 H) 2.15 (6 H)	0.81 (18 H)	
4-H ⁺	3.50	2.80 (6 H) 3.17 (6 H)	1.45	4.82
5	2.74 (4 H)	2.03 (3 H) 2.13 (6 H) 2.23 (3 H)	0.85 (18 H)	
5-H ⁺	3.51	2.77 (6 H) 3.15 (6 H)	1.40	4.77
6	2.78 (4 H)	2.14 (12 H)	0.85 (18 H)	
6-H ⁺	3.38	2.80 (6 H) 3.28 (6 H)	1.39	4.73

we found that hexaethylbenzene can be ipso alkylated with $\text{Me}_2\text{C}^+\text{H}$ as well as with Me_3C^+ in $\text{SbF}_5/\text{SO}_2\text{ClF}$ solution at low temperature. The β -methyl group of the ethyl substituent at the C_1 (ipso) carbon is shifted upfield in these benzenium ions 9, 10, reflecting a pseudoaxial confirmation similar to that previously observed for hexaethylbenzenium ions and for 1-3 in the present study. The methyl, methylene, and α -carbons of the isopropyl and *tert*-butyl groups in benzenium ions 9 and 10 showed exchange broadening even at -80°C . On increasing the

temperature (above -60°C), additional signals appeared (irreversible) and some decomposition occurred.

Attempts to alkylate hexaisopropylbenzene with $\text{Me}_2\text{C}^+\text{H}$ at low temperature was not successful, and under more forcing conditions at more elevated temperatures dealkylation and oligomerization were observed. On the other hand, protonation of hexaisopropylbenzene could be achieved by its slow addition to cold magic acid in SO_2ClF at -75°C under efficient mixing. The ^{13}C NMR spectrum of the resulting red solution is consistent with the formation of hexaisopropylbenzenium ion (11). The C_1 -carbon of 11 is observed at $\delta_{13\text{C}}$ 76.06 and is the most deshielded sp^3 -hybridized C_1 observed so far in hexaalkylbenzenium ions. It is deshielded by 17.86 ppm compared to the C_1 -carbon of hexaethylbenzenium ion ($\delta_{13\text{C}}$ 58.2).⁸

The crowded benzenium ions 8-10 exhibit slight nonequivalence of the C_3 , C_5 absorptions (meta) in the ^{13}C NMR spectra. For ion 11 the nonequivalence of both ortho (C_2 , C_6) and meta (C_3 , C_5) carbons is observed which is similar to the reported ^{13}C (CPMAS) NMR spectrum of the heptamethylbenzenium ion in the solid state.^{6,7}

Experimental Section

Isomerization of Hexaalkylbenzenes. To hexaethylbenzene (1 mmol) dissolved in anhydrous benzene (10 mL) was added AlCl_3 (1 mmol) with efficient magnetic stirring at 30°C . After 1 h the reaction mixture was quenched in ice/bicarbonate, extracted in ether, separated, dried (MgSO_4), and analyzed by GLC.

To the hexaalkylbenzene substrates 1-3 (1 mmol) in Freon-113 (20 mL) was added a solution of SbF_5 (1 mmol) in Freon-113 (5 mL) with efficient stirring at 0°C . The reaction was allowed to continue at room temperature overnight before workup and GC analysis.

To the hexaalkylbenzene substrates 1-6 (1 mmol) dissolved in Freon-113 (20 mL) was added with efficient stirring GaCl_3 (1 mmol) and a drop of water. After 16 h at 30°C the reaction was quenched in ice/bicarbonate, extracted as before, and analyzed by GC.

Table III. ^1H NMR Chemical Shifts^a for the Diethyltetramethylbenzenium Ions

ion ^b	proton chemical shifts and multiplicities ^a		
	H_1	CH_2	CH_3
1a-H ⁺	4.44, br	2.8-3.0 ^c	C_1 - CH_3 , 0.42, t; C_2 - CH_3 , 1.41, t; $\text{C}_{3,5}$ - CH_3 , 2.48, s; C_4 - CH_3 , 2.94, s; C_6 - CH_3 , 2.75, s
2a-H ⁺	4.33, br	2.8-3.0 ^c	C_1 - CH_3 , 0.38, t; $\text{C}_{2,6}$ - CH_3 , 2.76, s; C_3 - CH_3 , 1.28, t; C_4 - CH_3 , 2.93, s; C_5 - CH_3 , 2.41, s
3a-H ⁺	4.39, br	2.8-3.0 ^c	C_1 - CH_3 , 0.40, t; $\text{C}_{2,6}$ - CH_3 , 2.70, s; $\text{C}_{3,5}$ - CH_3 , 2.46, s; C_4 - CH_3 , 1.65, t

^a Proton chemical shifts are in ppm relative to external (capillary) Me_4Si multiplicities are given by s = singlet or t = triplet. ^b In $\text{HF-SbF}_5/\text{SO}_2\text{ClF}$ at -75°C . ^c Partially obscured by methyl resonances.

Table IV. Carbon-13 Chemical Shifts^a for the Diethyltetramethylbenzenium Ions

ion ^b	carbon-13 chemical shifts					alkyl
	C_1	C_2 , C_6	C_3 , C_5	C_4		
1a-H ⁺	61.9	196.3	141.5 141.1	193.4	C_1 - CH_2 , 32.3; C_2 - CH_2 , 29.2; C_1 - CH_3 , 7.6; C_2 - CH_3 , 12.9; $\text{C}_{3,5}$ - CH_3 , 14.6; $\text{C}_{4,6}$ - CH_3 , 23.2, 23.7	
2a-H ⁺	63.9	193.5 ^c 192.8 ^c	146.9, C_3 142.3, C_5	191.9 ^c	C_1 - CH_2 , 32.7; C_3 - CH_2 , 22.1; C_1 - CH_3 , 7.0; $\text{C}_{2,4,6}$ - CH_3 , 22.1, 22.7, 22.9; C_3 - CH_3 , 11.6; C_5 - CH_3 , 14.4	
3a-H ⁺	63.7	195.2	140.7	194.0	C_1 - CH_2 , 32.3; C_4 - CH_2 , 28.9; C_1 - CH_3 , 7.2; $\text{C}_{2,6}$ - CH_3 , 27.6; $\text{C}_{3,5}$ - CH_3 , 11.7; C_4 - CH_3 , 13.9	

^a Chemical shifts are in ppm relative to external (capillary) Me_4Si . ^b In $\text{HF-SbF}_5/\text{SO}_2\text{ClF}$ at -70°C . ^c Specific assignments uncertain.

Table V. Carbon-13 Chemical Shifts^a for Some Heptaalkylbenzenium Ions in $\text{SbF}_5/\text{SO}_2\text{ClF}$ or $\text{HF}\text{SO}_3\text{-SbF}_5(1:1)/\text{SO}_2\text{ClF}$

ion	temp, $^\circ\text{C}$	C_1	C_2 , C_6	C_3 , C_5	C_4	additional
7	-75	65.2	197.07	140.79	189.63	C_1 - $\text{CH}(\text{Me})_2$, 21.94; C_1 - $\text{CH}(\text{Me})_2$, 14.55; C_1 -Me, 16.78; $\text{C}_{2,6}$ -Me, 23.15
8	-55	67.8	188.80	146.76, 138.51	198.1	C_1 - $\text{C}(\text{Me})_3$, ^b 24.77; C_1 - $\text{C}(\text{Me})_3$, 16.97; C_1 -Me, 18.99; $\text{C}_{3,5}$ -Me, 14.09; $\text{C}_{2,6}$ -Me, 21.32; C_4 -Me, ^b 24.49
9	-70	71.03	138.34	147.1, 148.46	207.63	C_1 -Me, 8.3; remaining Me, 13-14; C_1 - $\text{CH}(\text{Me})_2$, 28.5; $-\text{CH}_2$, 25-26
10	-70	71.23	198.02	148.15, 153.98	207.60	C_1 -Me, 6.8; remaining Me 13-14; C_1 - $\text{C}(\text{Me})_3$, 31.5; $-\text{CH}_2$, 27-28
11	-70	76.06	213.44, 211.33	150.03, 131.71	202.67	C_1 - $\text{CH}(\text{Me})_2$, 34.49; C_1 - $\text{CH}(\text{Me})_2$, 16.99; $\text{C}_{2,6}$ - $\text{CH}(\text{Me})_2$, 37.97; $\text{C}_{2,6}$ - $\text{CH}(\text{Me})_2$, 19.79; $\text{C}_{3,5}$ - $\text{CH}(\text{Me})_2$, 33.60; $\text{C}_{3,5}$ - $\text{CH}(\text{Me})_2$, 18.79; C_4 - $\text{CH}(\text{Me})_2$, 36.37; C_4 - $\text{CH}(\text{Me})_2$, 20.63

^a Chemical shifts are in ppm relative to external Me_4Si . ^b Relative assignment uncertain.

Preparation of Ions. The protonation of arenes in HF-SbF_5 (1:1), $\text{FSO}_3\text{H-SbF}_5$ (4:1), and $\text{FSO}_3\text{H-SbF}_5$ (1:1) was analogous to the methods already described.⁸ For the reactions of isopropyl or *tert*-butyl cation with the substrates, the alkyl cation (2-3 equiv) was first generated from the halide precursor in $\text{SbF}_5/\text{SO}_2\text{ClF}$ and was then added slowly to a cold slurry (-75°C) of the aromatic compound (1 equiv) in SO_2ClF with efficient vortex mixing.

Nuclear Magnetic Resonance Spectra and GC Analyses. ^1H NMR spectra were obtained with a Varian Model A56/60A instrument equipped with a variable-temperature probe. ^{13}C NMR spectra were recorded on a Varian FT80 equipped with a low-temperature setup using external Me_4Si as reference or a Varian XL-200 instrument using acetone- d_6 as external lock and reference. GC analyses were performed on a Varian Model 3700 gas chromatograph with a 50-m capillary column (OV101) and an on-line automatic integrator.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged. We thank Professor Melvin Newman of the Ohio State University for samples of diethyl- and dineopentyltetramethylbenzene isomers⁹ as well as Professor R. Grubbs and Dr. Ken Dooxse of Cal. Tech. for a sample of hexaisopropylbenzene.¹⁰

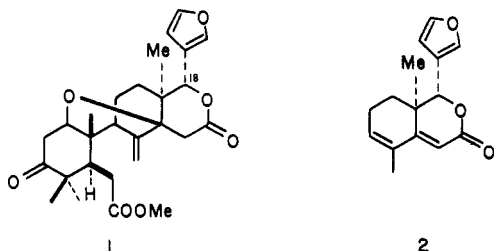
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A Short Synthesis of *dl*-*epi*-Pyroangolensolide and *dl*-Pyroangolensolide: Confirmation of the Structures of Pyroangolensolide and Calodendrolide

Siegfried E. Drewes,¹ Paul A. Grieco,* and John C. Huffman
Department of Chemistry, Indiana University, Bloomington,
Indiana 47405

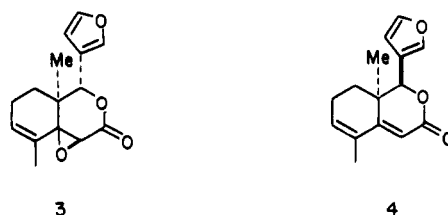
Received September 21, 1984

Pyroangolensolide, obtained from pyrolysis at 305°C of methyl angolensate (1), has been assigned structure 2 on the basis of spectral data (IR, ^1H NMR, MS, UV, and CD).² The configuration about the carbon [C(18), limo-



noid numbering] bearing the α -oriented furan ring in structure 2 is based solely on a positive Cotton effect which is similar in profile and position to that of methyl angolensate. Pyroangolensolide has also been obtained by treatment of calodendrolide (3), a naturally occurring

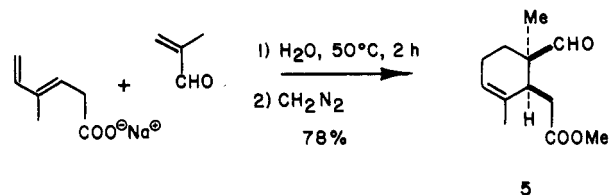
C_{15} -degraded limonoid,⁴ with hydriodic acid. It should



be pointed out that the structure assigned to calodendrolide is based on its conversion into pyroangolensolide. In view of the harsh conditions which were employed above for the formation of pyroangolensolide, and the fact that the configuration at C(18) in structure 2 rests solely in its optical rotatory dispersion curve, we set out to prepare both *dl*-pyroangolensolide and *dl*-*epi*-pyroangolensolide (cf. structure 4). We detail below a short synthesis of racemic 2 and 4, both crystalline, which, via single-crystal X-ray analysis, unambiguously established the structure of pyroangolensolide as 2 and confirmed the structural assignment put forth by Cassady and Lui for calodendrolide.

Tokoroyama and co-workers⁸ have published an eight-step synthesis of *dl*-pyroangolensolide and *epi*-pyroangolensolide. Physical data, including a detailed ^1H NMR analysis of 2 and 4 are provided; however, in the absence of a single-crystal X-ray analysis of either 2 or 4, the complete structural assignments for pyroangolensolide and *epi*-pyroangolensolide remain suspect.

Our synthesis of *dl*-pyroangolensolide and *dl*-*epi*-pyroangolensolide, which was carried out via a four-step sequence, features an aqueous Diels-Alder reaction.⁹ Condensation of sodium 4-methyl-3(*E*),5-hexadienoate¹⁰



with methacrolein in water (50°C , 2 h) afforded after esterification with ethereal diazomethane a 78% isolated yield of the endo Diels-Alder adduct 5. Less than 5% of the exo adduct 6 could be detected by ^1H NMR analysis of the crude reaction product. Addition of 3-furyllithium in tetrahydrofuran-ether (3:4) to aldehyde 5 gave rise to a mixture of lactones 7 and 8 in a ratio of 4:1. In contrast, Tokoroyama and co-workers reported that addition of 3-furyllithium to 9 gives rise directly to a mixture of *dl*-pyroangolensolide and *dl*-*epi*-pyroangolensolide in a ratio of 7:3. Note, the structures of 7 and 8 follows from a single-crystal X-ray analysis of our synthetic *dl*-*epi*-pyroangolensolide (vide infra).

(4) Limonoids⁵ comprise a large class of C_{26} degraded triterpenes which, apart from their bitter taste, possess insect antifeedant⁶ and limited antitumor properties.⁷

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