A SHORT SYNTHESIS OF (±)-2,5-EPOXY-6(E),8(E)-MEGASTIGMADIENE

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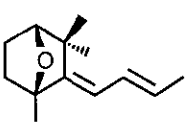
Abstract - (±)-2,5-Epoxy-6(E),8(E)-megastigmadiene **1** was synthesized in seven steps and 27% overall yield from 2-methylfuran. The Diels-Alder reaction of 2-methylfuran with 2-chloroacrylonitrile gave 2-chloro-2-cyano-1-methyl-7-oxabicyclo[2.2.1]hept-5-ene **5a** as the major regioisomer. Hydrogenation of **5a** followed by hydrolysis and alkylation provided the key intermediate, 1,3,3-trimethyl-7-oxabicyclo[2.2.1]heptan-2-one **4**. The conjugated diene sidechain was then introduced via a Grignard reaction followed by formation and subsequent decomposition of the phenylurethane derivative **10** to give **1** and its 6(Z) isomer **2**.

While not considered ubiquitous throughout plant-derived natural products, the 1,3,3-trimethyl-7-oxabicyclo[2.2.1]heptane system is found as a major component of a number of interesting compounds. Among these are 2,5-epoxymegastigma-6(E),8(E)-diene **1**[1] and its 6(Z) isomer **2**[1] and 3',6'-epoxycycloaurapten **3**.[2] Previous syntheses of **1-3** have left creation of the oxygen bridge of the 7-oxabicyclo[2.2.1]heptane moiety as a late step in the synthesis, contributing to low yields and mixtures of products.[1,3,4] In one sense, it is strange that no synthesis of **1-3** has employed the intermolecular Diels-Alder reaction to construct the 1,3,3-trimethyl-7-oxabicyclo[2.2.1]heptane moiety. However, there is evidence in the literature that 2-methylfuran is a poor diene in the Diels-Alder reaction, and undergoes aromatic substitution reactions with appropriate dienophiles preferentially.[5,6] This has prompted several groups to approach the synthesis of 1-methyl-7-oxabicyclo[2.2.1]heptanes via intramolecular Diels-Alder reactions in which the dienophile is tethered to a 1-methylene carbon.[7-10] The advantage to this approach is the regiocontrol inherent in the intramolecular Diels-Alder reaction. The disadvantage to this approach is the necessity of removing the tethering functional group to form the 1-methyl group.



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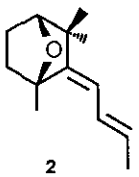

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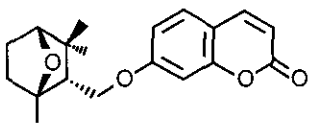

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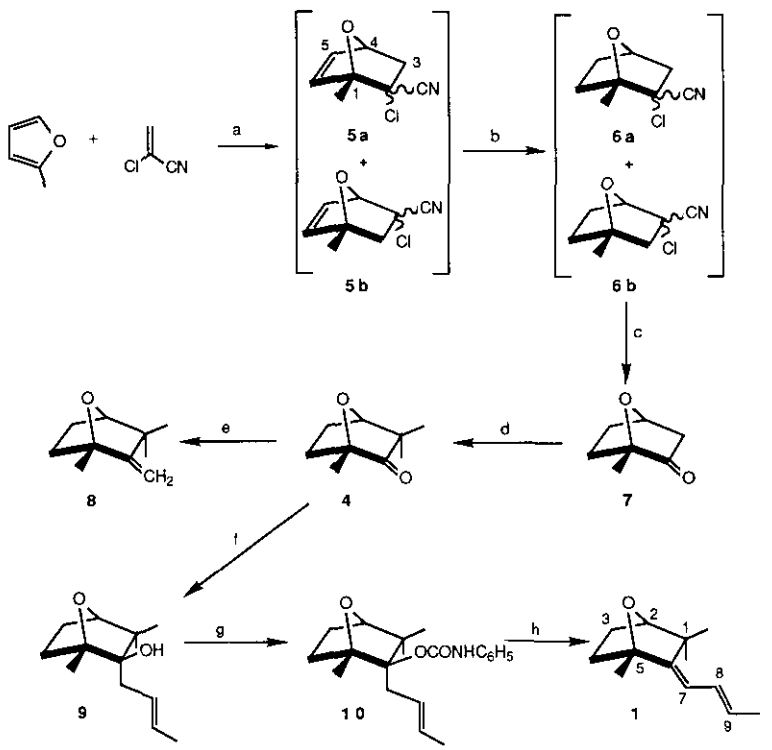
A long-standing interest in the intermolecular Diels-Alder reactions of furans led us to examine a synthetic route to **1** and **2** via an intermolecular Diels-Alder reaction with 2-methylfuran as the diene component. In spite of the aforementioned reports that 2-methylfuran is a poor diene, 2-methylfuran has been used successfully in the intermolecular Diels-Alder reaction with maleic anhydride under normal conditions to give reasonably high yields of the adduct.[11] Exploration of a route based on this reaction indicated that the transformations required to convert the two carbonyl groups of the anhydride moiety into the required structural features of **1** and **2**

would be long and lead to very low yields of the targets. After exploring the viability of several other dienophiles, including 3,3-dimethylacryloyl chloride, crotonaldehyde, and acrylonitrile, in the intermolecular Diels-Alder reaction with 2-methylfuran, attention was turned to the use of the ketene equivalent, 2-chloroacrylonitrile. Use of this dienophile suggested an approach in which the key intermediate in the synthesis would be 1,3,3-trimethyl-7-oxabicyclo[2.2.1]heptan-2-one **4**. 2-Chloroacrylonitrile has been used successfully in the intermolecular Diels-Alder reaction with furans, both at high pressure and at normal pressures.[12,13] In fact, the reaction of 2-chloroacrylonitrile with 2-methylfuran has been reported to give a 62% yield of the adduct after 4 weeks at 4°C.[14] However, attempts to repeat this experiment led only to very low yields (ca. 15%) of the desired adduct. Other reports in the literature indicated that Lewis acid catalysis using cupric tetrafluoroborate[15] or zinc iodide[16] promoted the intermolecular Diels-Alder reaction of 2-chloroacrylonitrile with furan. Lewis acid catalysis of the reaction of 2-chloroacrylonitrile with 2-methylfuran using cupric tetrafluoroborate did not significantly improve the yield of the desired adduct, but the use of zinc iodide did give vastly improved results.

Initially, the reaction of 2-methylfuran with 2-chloroacrylonitrile in the presence of a catalytic amount of zinc iodide required one month at 0°C under nitrogen to form the Diels-Alder adduct, as a mixture of regio- and stereoisomers (**5a** + **5b**), in 79% yield. The time was reduced to two weeks in subsequent runs with little difference in yield. As expected, the adduct was not particularly stable at room temperature, readily undergoing a reverse Diel-Alder reaction to return starting materials. To overcome this problem, the adduct was dissolved in ethyl acetate, filtered to remove the residual zinc iodide, and hydrogenated to remove the 5,6 double bond. The saturated adduct, obtained in 79% overall yield, was more stable but was still an inseparable mixture of regio- and stereoisomers (**6a** + **6b**).

Rather than resort to extensive chromatographic separations to purify the mixture of the saturated adduct, the decision was made to carry on the mixture through the next step, hydrolysis to the ketone. The method of Shiner et al.[17] was employed for this conversion. The mixture of saturated adducts (**6a** + **6b**) was heated with potassium hydroxide in t-butanol for 11 hours. Neutralization and removal of the t-butanol followed by distillation at reduced pressure gave 1-methyl-7-oxabicyclo[2.2.1]heptan-2-one **7** as the principle product (76% yield). The regiochemistry of **7** was established by examination of the COSY spectrum. The bridgehead proton (4-H) at 4.78 ppm was clearly coupled to the 3β-H at 2.5 ppm and the 5β-H at 2.07 ppm. Coupling of the 4-H to the 3α-H and 5a-H was not seen. Coupling of the bridgehead proton to the protons on the carbon adjacent to the carbonyl would not be evident if the carbonyl moiety was located at C-3. Thus, **7** must have the desired regiochemistry.

Alkylation of **7** with two equivalents of methyl iodide was accomplished using potassium t-butoxide in t-butanol at room temperature for 48 hours to give **4** in 85% yield. Addition of the sidechain at C-2 was envisioned originally as a Wittig reaction. This reaction was approached with some trepidation since the carbonyl moiety of **4** is quite hindered. As it turned out, this trepidation was justified. While **4** reacted readily with the ylide formed from methyltriphenylphosphonium bromide and n-butyllithium to give 2-methylene-1,3,3-trimethy-7-oxabicyclo[2.2.1]heptane **8** in 81% yield, no product was obtained when the ylide formed from (2-butenyl)triphenylphosphonium bromide was used in this reaction. Attempts to employ Emmons-Horner and other conditions to form the exocyclic diene in one step were also unsuccessful. Consequently, a two step sequence involving an addition of the side chain



a) ZnI_2, neat, 0°C, 14 days; b) H_2/Pd-C, EtOAc; c) KOH, t-BuOH-H_2O, 50°C; MeI, K^+t-BuO^-, THF; e) $Me(C_6H_5)_3P^+Br^-$, n-BuLi, THF; f) C_4H_7MgBr, Et_2O, reflux; g) C_6H_5NCO, pyridine, 72 h; h) 225°C, $-CO_2$, $C_6H_5NH_2$.

followed by elimination to form the exocyclic double bond was devised. The addition step was envisioned as a straightforward Grignard reaction. The Grignard reagent formed from 1-bromo-2(E)-butene was reacted with **4** at reflux for 8 hours to give 2-(2-(E)-butenyl)-1,3,3-trimethyl-7-oxabicyclo[2.2.1]heptan-2-ol **9** in 83% yield. No attempt was made to determine the stereochemistry of the addition, but addition of the Grignard reagent appeared to be from the alpha face from inspection of the ^1H nmr data.

With **9** in hand, it was anticipated that elimination of water to give the exocyclic double bond would be relatively easy. This assumption was based upon two structural features; the alcohol to be eliminated was tertiary and the anticipated elimination could occur in only one direction since two of the three carbons bonded to the tertiary site were quaternary. Unfortunately, this assumption was also unwarranted. Simple heating of **9**, either neat or in solution, failed to cause dehydration. It was necessary to avoid strongly acidic conditions, conditions which are typically used for dehydration, since the oxygen bridge is susceptible to ring opening and elimination *in our experience with this class of compounds.* However, catalysis with p-toluenesulfonic acid in refluxing benzene was tried, again without success. Other dehydration conditions such as thionyl chloride-pyridine-heat, p-toluenesulfonyl chloride-pyridine-heat, and acetic anhydride-pyridine-heat also failed to cause dehydration, returning starting material in most cases. At this point, we began to wonder about the reactivity of the tertiary hydroxyl group of **9**. To better explore this reactivity, we attempted to prepare the phenylurethane derivative of **9** by reaction with phenyl isocyanate. Reaction of **9** with phenyl isocyanate neat at room temperature or

with heat, fairly standard conditions for tertiary alcohols, failed to give the anticipated derivative, again returning starting material. However, heating **9** with phenyl isocyanate at reflux in very dry pyridine gave, after one week, the phenylurethane derivative **10** in 82% yield.

In one sense, the preparation of **10** in high yield was surprising since tertiary alcohols often undergo dehydration with phenyl isocyanate. In this case, no **1** or **2** was obtained. However, after melting, continued heating of the sample caused rapid evolution of bubbles, indicating that decarboxylation was occurring. Consequently, **10** was pyrolyzed at 225°C causing elimination of CO_2 and aniline and giving a mixture of **1** and **2** in a ratio of 3.5:1, respectively. This result was expected from potential energy calculations which show the 6(E),8(E) isomer **1** to be approximately 1 Kcal/mol more stable than the 6(Z),8(E) isomer **2**.[18] Separation of the isomers by column chromatography resulted in the isolation of pure **1** (78% yield from **10**). The ir, nmr, and ms data were essentially identical with reported values.[3]

Thus, (±)-2,5-epoxy-6(E),8(E)-megastigmadiene has been synthesized from 2-methylfuran in 27% overall yield, and the intermolecular Diels-Alder reaction using 2-methylfuran has been demonstrated to be a viable method for synthesizing natural products containing the 1,3,3-trimethyl-7-oxabicyclo[2.2.1]heptane system in relatively high yield. The major drawback to this approach is, of course, that the synthesis is not a chiral synthesis. Work is currently in progress to apply this route to the synthesis of other natural products.

EXPERIMENTAL

General Experimental Procedures. - Ir spectra were recorded on a Perkin-Elmer Model 1600 FTIR spectrophotometer. ^1H and ^{13}C nmr spectra were obtained using a GE QE-300 NMR at 300 MHz and 75.6 MHz, respectively, with tetramethylsilane as an internal standard. Mass spectra were recorded using a Hewlett-Packard Model 5988A GC/MS coupled with a Hewlett-Packard 59970 MS Chemstation. Injection port and column oven temperatures were 225 °C and 250 °C, respectively. Melting points were obtained on a Fischer-Johns melting point apparatus and are uncorrected. Silica gel refers to Silica gel 60 G (EM Labs). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

2-Chloro-2-cyano-1-methyl-7-oxabicyclo[2.2.1]heptane, **6a** + 3-Chloro-3-cyano-1-methyl-7-oxabicyclo[2.2.1]heptane, **6b**. - In a typical run, zinc iodide (0.65 g, 2.04 mmol) was added to a solution of 2-chloroacrylonitrile (5.28 g, 60.3 mmol) and 2-methylfuran (5.51 g, 67.1 mmol). The yellow solution was stirred for 14 days at 0°C under nitrogen in the absence of light. The mixture was diluted with ethyl ether (50 ml), washed successively with 1N $NaHCO_3$ (2 x 50 ml), saturated NaCl (1 x 50 ml), and dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to give 8.11 g (79%) of a dark yellow oil (**5a** + **5b**). The products of several runs were combined to carry on to the next step. The isomeric mixture of **5a** and **5b** (35.64 g, 210 mmol) was dissolved in ethyl acetate (100 ml), filtered to remove any residual zinc iodide, and 5% Pd-C catalyst (2.15 g) was added to the solution. The mixture was hydrogenated using a Parr apparatus at 45 psi for 9 h. The Pd catalyst was removed by filtration through Celite and the yellow filtrate was concentrated in vacuo to give a yellow oil. Distillation using a Kugelrohr apparatus gave a mixture of **6a** + **6b** (ca. 3:1 by nmr) as a colorless oil, 36.01 g (100%, 79% from 2-methylfuran): bp 98°C (0.2 mm); ir (film) 2930, 2860, 2215, 1435, 1375, 1125 cm^{-1}; ^1H nmr (**6a**) ($CDCl_3$) δ 4.57 (dd, J= 4.5,4.5 Hz, 1H, C4-H), 2.83 (ddd, J = 13.6, 5.8, 2.7 Hz, 1H, C3-H), 2.45 (m, 1H, C5-H), 2.01 (d, J=13.6 Hz, 1H, C3-H), 1.89 (m, 1H, C5-

H), 1.69-1.5 (m, 2H, C6-H_2), 1.63 (s, 3H, C1-CH_3); ^{13}C nmr (**6a**) ($CDCl_3$) 16.69 q (C1-CH_3), 30.12 t (C6), 31.55 t (C5), 48,95 t (C3), 78.66 d (C4), 88.96 s (C1), 118.91 s (C2).

1-Methyl-7-oxabicyclo[2.2.1]heptan-2-one, **7**. - A solution of **6a** + **6b** (25.37 g, 0.148 mol) in tetrahydrofuran (20 ml) was added dropwise to a stirred solution of potassium hydroxide (21.26 g, 0.38 mol) in t-butanol (100 ml) and water (12 ml) at 50°C over 1 h. The dark solution was stirred an additional 0.5 h at 50°C and then heated at reflux for 10 h with vigorous stirring. The burgundy-colored solution was cooled to room temperature and diluted with petroleum ether (35-50°C, 100 ml). The mixture was washed with 5% $NaHCO_3$ (3 x 50 ml) and water (5 x 100 ml) and dried over anhydrous $MgSO_4$. The solvent was removed by fractional distillation, and the residue was distilled in a Kugelrohr apparatus to give **7** as a clear, colorless liquid, 14.24 g (76%): bp 53°C (0.75 mm); ir (film) 2975, 2930, 1750, 1440, 1110 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 4.79 (dd, J= 5.7,5.7 Hz, 1H, C4-H), 2.52 (ddd, J= 17.3, 5.9, 2.7 Hz, 1H, C3β-H), 2.11 (d, J= 17.4 Hz, 1H, C3α-H), 2.08 (m, 1H, C5β-H), 1.75-1.64 (m, 3H, C5α-H, C6-H_2), 1.47 (s, 3H, C1-CH_3); ^{13}C nmr ($CDCl_3$) 14.03 q (C1-CH3), 30.0 t (C6), 30.28 t (C5), 44.57 t (C3), 74.48 d (C4), 85.06 s (C1), 212.72 s (C2); Elms m/z (relative intensity) 126 (8), 109 (1), 98 (100), 83 (35), 71 (5), 55 (29). Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.41; H, 8.11.

1,3,3-Trimethyl-7-oxabicyclo[2.2.1]heptan-2-one, **4**. - To a stirred solution of **7** (8.84 g, 70.2 mmol), methyl iodide (35.79 g, 252 mmol) in freshly distilled tetrahydrofuran (100 ml) was added a solution of potassium t-butoxide (20.17 g, 180 mmol) in tetrahydrofuran (100 ml) dropwise over 1 h at 0°C under nitrogen. The mixture was then allowed to warm to room temperature and stirred vigorously for 48 h. Unreacted methyl iodide was removed by distillation. The solution was cooled to room temperature and washed with 100 ml H_2O. The aqueous layer was extracted with ethyl ether (2 x 50 ml), and the combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was distilled in a Kugelrohr apparatus to give **4** as a clear liquid, 9.15 g (85%): bp 42°C (0.3 mm); ir (film) 2934, 2868, 1760, 1602, 1115 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 4.12 (d, J = 4.8 Hz, C4-H), 1.80 (m, 2H, C5-H_2), 1.49 (m, 2H, C6-H_2), 1.30 (s, 3H, C1-CH_3), 1.06 (s, 3H, C3-βCH_3), 0.79 (s, 3H, C3-αCH_3); ^{13}C nmr ($CDCl_3$) 14.59 q (C1-CH_3), 19.82 q (C3-CH_3), 22.69 (C3-CH_3), 25.34 t (C6), 30.95 t (C5), 48.69 s (C3), 83.47 d (C4), 85.82 s (C1), 217.88 s(C2); Elms m/z (relative intensity) 154 (4), 126 (100), 111 (86), 108 (69), 93 (57), 83 (74), 69 (63), 55 (59).

1,3,3-Trimethyl-2-methylenyl-7-oxabicyclo[2.2.1]heptane, **8**. - To a solution of methyltriphenylphosphonium iodide (10.35 g, 25.6 mmol) in tetrahydrofuran (100 ml) under nitrogen at 0°C was added 17 ml of 1.6M n-butyllithium in hexane. The yellow solution was allowed to warm to room temperature over 4 h, at which point the solution turned red. To this solution was added a solution of **4** (3.48 g, 22.3 mmol) in tetrahydrofuran (25 ml), and the resulting mixture was stirred for 48 h. A white precipitate was removed by gravity filtration to give a light orange colored filtrate which was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by distillation in a Kugelrohr apparatus to give **8** as a clear colorless liquid, 2.74 g (81%): bp 35°C (0.2 mm); ir (film) 3050, 2950, 2850, 1660, 1445, 1180 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 4.63 (s, 1H, C8-H), 4.51 (s, 1H, C8-H), 3.89 (d, J= 5.1Hz, 1H, C4-H), 1.79 (m, 1H, C6-H), 1.67 (m, 1H, C5-H), 1.38-1.52 (m, 2H, C5-H, C6-H), 1.42 (s, 3H, C1-CH_3), 1.03 (s, 3H, C3-CH_3), 1.01 (s, 3H, C3-CH_3); ^{13}C nmr ($CDCl_3$) 18.30 q (C1-CH_3), 23.75 q (C3-CH_3), 25.84 q (C3-CH_3), 28.66 t (C5), 35.65 (C6), 45.83 s (C3), 84.46 d (C4), 86.41 s (C1), 97.96 t (C8), 100.31 s (C2); Elms m/z (relative intensity) 152 (29), 137 (29), 123 (26), 109 (100), 93 (26), 81 (32), 69 (34), 55 (11).

2-(2-*E*-butenyl)-1,3,3-trimethyl-7-oxabicyclo[2.2.1]heptan-2-ol, **9**. - A solution of trans-crotyl bromide (20.31 g, 150 mmol) in anhydrous ethyl ether (15 ml) was added slowly to a stirred mixture of magnesium pellets (6.33 g, 260 mmol) in ethyl ether (50 ml) under nitrogen. The mixture turned dark gray within 30 min and was heated to reflux for an additional 2 h. The solution was cooled to room temperature and a solution of freshly distilled **4** (9.04 g, 58.7 mmol) in ethyl ether (25 ml) was added dropwise. The mixture was stirred at room temperature for 4 h and then heated at reflux for 8 h. The mixture was cooled to 0°C and quenched with 1N NH_4Cl (50 ml). The organic layer was removed, and the aqueous layer was extracted with ethyl ether (3 x 50 ml). The combined ether layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was distilled in a Kugelrohr apparatus and the major fraction was subjected to column chromatography over silica gel eluted with chloroform to give 10.28 g (83%) of **9** as a clear liquid: bp 72°C (2 mm); ir (film) 3450, 3060, 2950, 1620, 1440, 1105 cm^{-1}; ^1H nmr ($CDCl_3$) δ 6.30 (br s, 1H, OH), 5.65 (m, 1H, C2'-H), 5.50 (m, 1H, C3'-H), 3.75 (t, J= 5.4 Hz, 1H, C4-H), 2.34 (m, 2H, C1'-H), 1.57-1.85 (m, 4H, C5-H_2, C6-H_2), 1.61 (d, J= 6.9 Hz, 3H, C3'-CH_3), 1.31 (s, 3H, C5-CH_3), 1.10 (s, 3H, C3-βCH_3), 0.80 (s, 3H, C3-αCH_3); Elms m/z (relative intensity) 210 (1), 195 (37), 167 (14), 155 (15), 137 (33), 109 (95), 95 (21), 83 (100), 55 (50).

Phenylurethane Derivative (**10**) of **9**. - To a solution of freshly distilled **9** (3.14 g, 14.9 mmol) in dry pyridine (50 ml) at 0°C under nitrogen were added 8 ml (1.93 g, 16.2 mmol) of phenyl isocyanate in dry pyridine (25 ml). The yellow colored mixture was stirred at room temperature for 72 h, cooled to 0°C, and quenched with water (25 ml). The mixture was diluted with ethyl ether (50 ml), and the aqueous layer was separated and washed with ethyl ether (3 x 40 ml). The combined ether layers were washed successively with 1N $NaHCO_3$ (50 ml), 1N $CuSO_4$ (5 x 50 ml), and saturated NaCl (2 x 50 ml). The ether layer was dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The residue was distilled in a Kugelrohr apparatus and the major fraction was subjected to column chromatography over silica gel eluted with chloroform to give **10** as a yellow solid, 4.05 g (82%): mp 185°C; ir (neat) 3295, 3120 2950, 1685, 1590, 1430, 1095 cm^{-1}; ^1H nmr ($CDCl_3$) δ 7.25 (m, 5H, ArH), 6.49 (br s, 1H, NH), 5.34-5.45 (m, 2H, C2'-H, C3'-H), 3.72 (d, J = 5.5 Hz, 1H, C4-H), 3.07 (m, 1H, C1'-H), 2.53 (m, 1H, C1'-H), 2.02-1.58 (m, 3H, C5-H_2, C6-H), 1.56 (s, 3H, C1-CH_3), 1.53 (br, 3H, C10-H), 1.29 (m, 1H, C6-H), 1.16 (s, 3H, C3-βCH_3), 1.01 (s, 3H, C3-αCH_3); ^{13}C nmr ($CDCl_3$) 19.18 q (C1-CH_3), 21.13 q (C3-CH_3), 25.57 q (C3-CH_3), 25.90 t (C6), 26.22 q (C3'-CH_3), 28.82 t (C1'), 32.18 t (C5), 48.76 s (C3), 86.36 d (C4), 90.26 s (C1), 90.48 s (C2), 119.09 d, 123.53 d, 125.92 d, 128.95d, 138.05 s, 152.03 s (OCONH).

(±)-2,5-Epoxymegastigma-6(*E*),8(*E*)-diene, **1**. - Phenylurethane derivative **10** (1.45 g, 4.4 mmol) was heated to 225°C in the Kugelrohr apparatus at atmospheric pressure. The crude diene distilled as the initial fraction. GC-MS analysis of the crude diene mixture showed it to be a 3.5:1 ratio of the two dienes. Separation of **1** from **2** was achieved by coloumn chromatography over silica gel eluted with ethyl acetate:pentane (1:12). The pure diene **1** was obtained as a yellow oil, 0.66 g (78%): bp 66°C (0.2 mm); ir (film) 3035, 2960, 2860 1600, 1440, 1110 cm^{-1}; ^1H nmr ($CDCl_3$) δ 6.20 (ddq, J= 11.8,11.3,1.8 Hz, 1H, C8-H), 5.81 (d, J= 11.8 Hz, 1H, C7-H), 5.43 (dq, J= 11.3,7.0 Hz, 1H, C9-H), 3.83 (d, J= 5.0 Hz, 1H, C2-H), 1.68 (dd, J= 7.0,1.8 Hz, 3H, C9-CH_3), 1.48-1.87 (m, 4H, C3-H_2, C4-H_2), 1.47 (s, 3H, C5-CH_3), 1.19 (s, 3H, C1-CH_3), 1.18 (s, 3H, C1-CH_3); ^{13}C nmr ($CDCl_3$) 19.05 q (C5-CH_3), 23.80 q (C1-CH_3), 26.09 q (C9-CH_3), 26.94 q (C1-CH_3), 29.88 t (C4), 35.89 t (C3), 45.74 s (C1), 85.89 d (C2), 88.96 s (C5), 110.53 d (C9), 113.76 s (C6), 125.11 d (C7), 128.52 d (C8); Elms m/z (relative intensity) 192 (27), 177 (6), 149 (14), 123 (49), 121 (28), 109 (46), 91 (29), 81 (34), 69 (84), 55 (16).

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