

Juvenile hormone analogues active on mosquitoes : Synthesis and biological activity of hydrocarbon juvenoids with a pinene and substituted cyclohexane ring in the terminal position

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Received 11 February 1999; accepted 15 July 1999

1-(2-Pinen-10-yl)-3,7-dimethyl-2(*E*), 6-octadiene **1**, 1-(2'-isopropyl-5'-methylcyclohexyl)-3,7-dimethyl-2(*E*),6-octadiene **2** and their analogues have been prepared. These compounds have been tested on *Culex pipiens quinquefasciatus* Say for their juvenile hormone (JH) activity.

Juvenile hormone analogues are being tested in various laboratories for their potential use as mosquito larvicides and for the control of insect pests¹. Most of these compounds induce morphogenetic effects which eventually result in some or complete inhibition of adult emergence. Juvenile hormone analogues also appear to influence survival of the emerged adults and their reproduction in a profound way^{2,3}. The biological activity of juvenile hormone (JH) analogues mainly depends on their chemical structures and stabilities. Most of the active compounds contain at least part of a branched carbon chain characteristic of isoprenoids. The presence of ethylenic bonds has also great significance in biological activity of juvenoids. In continuation of our work on insect juvenile hormone mimics chemistry^{4,5}, we herein report the synthesis and biological activity of geranyl-pinene, geranyl-menthyl hydrocarbons and their derivatives.

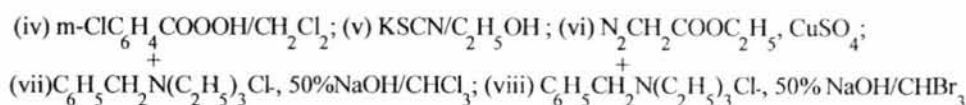
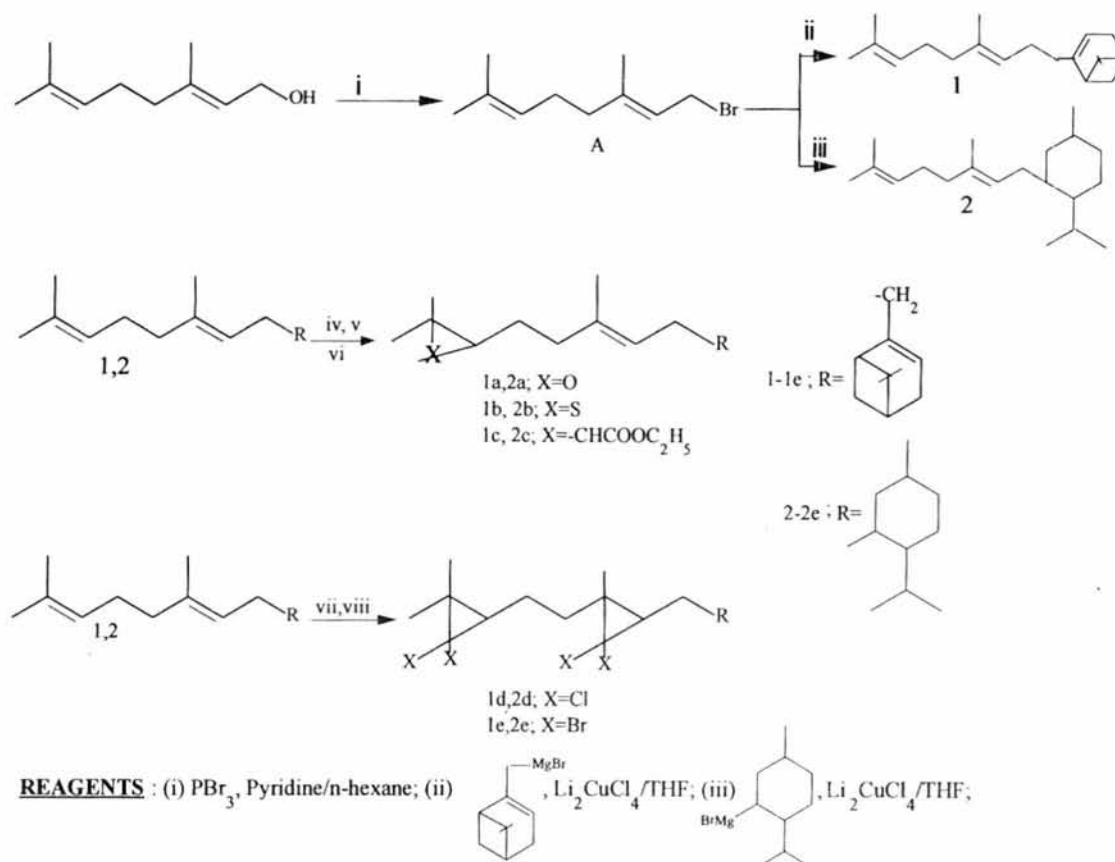
Results and Discussion

Geraniol, on treatment with PBr₃/pyridine in dry *n*-hexane at -10°C afforded geranyl bromide **A**. Myrtenol^{6,7} (prepared from SeO₂ oxidation of α -pinene in anhydrous ethanol followed by lithium aluminium hydride reduction in dry ether at 0°C), on reaction with PBr₃/pyridine in dry carbon tetrachloride at 0°C afforded myrtenyl bromide. Coupling⁸ of **A** with myrtenyl magnesium bromide under N₂ atmosphere at -10°C using catalytic amount of Li₂CuCl₄ in dry THF furnished 1-(2-pinen-10-yl)-3,7-dimethyl-2(*E*), 6-octadiene **1** in 61% yield. Menthol was brominated with PBr₃/pyridine in dry ether at 0°C to afford menthyl bromide. Dilithium

tetrachlorocuprate catalysed coupling reaction of menthyl magnesium bromide with **A** in dry THF at -10°C furnished 1-(2'-isopropyl-5'-methylcyclohexyl)-3,7-dimethyl-2(*E*),6-octadiene **2** in 44% yield after chromatographic purification. Treatment of hydrocarbons **1** and **2** with equimolar amount of *m*-chloroperbenzoic acid⁹ in dry CH₂Cl₂ gave mono epoxy derivatives **1a** and **2a** in 74.5% and 81.4% yield respectively. Oxiranes **1a** and **2a** on reaction with KSCN¹⁰ in ethanol afforded corresponding thirane derivatives **1b** and **2b** in good yields. Reaction of **1** and **2** with ethyl diazoacetate in the presence of copper sulphate furnished 1-(2-pinen-10-yl)-3,7-dimethyl-6,7-carbethoxymethylene-2(*E*)-octene **1c** and 1-(2'-isopropyl-5'-methylcyclohexyl)-3,7-dimethyl-6,7-carbethoxymethylene-2(*E*)-octene **2c**. Phase transfer catalysed reaction¹¹ of **1** and **2** with CHCl₃/CHBr₃ in the presence of aqueous NaOH gave bis-dichloro-methylene **1d** and **2d** and bis-dibromomethylene **1e** and **2e** derivatives (Scheme I). The spectral data (IR, ¹H NMR) of the synthesized compounds were consistent with their structures.

Juvenile hormone activity

The compounds (**1**, **1a-e**, **2**, **2a-e**) were tested for their juvenile hormone activity against *Culex pipiens quinquefasciatus*¹² Say. The 4th instar larvae of mosquitoes were reared in different doses of the compound for 24hr. Their mortality at larval, pupal and adult stages was noted. To find out the activity index, different grades were given to deaths at each stage, the larvae which died at larval stage only i.e. failed to moult to pupae, was rated as three. The larvae which succeeded in moulting into pupae but



Scheme I

failed to emerge as an adult, was rated as two and the pupae which did emerge into adult but failed to survive, was rated as one. The larvae which successfully reached the adult stage and survived for one day, was rated as zero. The activity index was determined by multiplying the number of larvae at one stage by its numerical value and dividing it by the total number of larvae taken into account. All the experiments were repeated six times with different concentrations to take out the mean mortality at each stage. With all the test chemicals, the mortality increased with the increase of dose of the chemical. The death in doses of 10ppm and 5ppm was on account of larvicidal effect of the chemical and on the account of formation of larval-pupal juvenoids and pupal-adult juvenoids, but with lower doses of 2ppm, 1ppm and 0.5ppm the death was only due to juvenoid formation having characters of larval-pupal intermediates and pupal-adult intermediates.

Entomological studies of compounds (1-1a-e, 2-2a-e) along with commercially available JHA-methoprene (standard) have been reported in Table I.

Experimental Section

Progress of all the reactions was monitored by TLC using Acme, silicagel impregnated with 13% CaSO₄. Silica gel (100-200 mesh) was used for column chromatography. ¹H NMR spectra (CCl₄) were recorded on a Varian 60 MHz spectrophotometer and Varian EM-390 spectrophotometer using tetramethylsilane as an internal standard (chemical shifts in δ , ppm and IR spectra (neat) were run on Perkin-Elmer 1430 spectrophotometer ($\nu_{\max}$ in cm⁻¹). Unless otherwise stated, all organic extracts were dried over anhydrous sodium sulphate.

1-(2-Pinen-10-yl)-3, 7-dimethyl-2 (E), 6-octadiene 1. To the Grignard reagent [prepared from myrtenyl bromide (2.15g, 10 mmoles) and activated

Mg turnings (0.24 g, 10 mmoles) in dry THF (15 mL) under N₂ atmosphere was added geranyl bromide (2.17g, 10 mmoles) in dry THF(15 mL) dropwise at -10°C. After stirring for 1 hr, Li₂CuCl₄ (2mL) was added to it. The reaction mixture was stirred for 3hr at -10°C and 12 hr at room temperature. The reaction mixture was then quenched with saturated NH₄Cl solution, extracted with ether (4 × 30 mL) washed with brine and dried. Solvent removal followed by chromatography over silica gel using pet. ether as eluent gave pure **1** (1.65 g, 61 %). R_f 0.678 in pet ether; IR (neat) : 2920, 1670, 1640, 1110, 910, 890, 790, 660 cm⁻¹; ¹H NMR: δ 0.9 (m, 3H, CH₃-C-CH₃), 1.25 (3H, CH₃-C-CH₃), 1.6(d,12H, J=9Hz, 3×CH₃-C=C, 1×CH, 1×CH₂), 1.9-2.25, (bs,11H, 5×CH₂-C=C, 1×CH-C=), 5-5.3 (bs, 3H, 3×H-C=C);

Anal.Calcd for C₂₀H₃₂: C, 88.16; H, 11.84. Found: C,88.05; H, 11.68%.

1-(2'-Isopropyl-5'-methylcyclohexyl)-3, 7-dimethyl-2(E),6-octadiene 2. To the Grignard reagent, [prepared from menthyl bromide (2.19 g, 10 mmoles) and activated Mg turnings (0.24 g, 10 mmoles) in dry THF (15 mL) under N₂ atmosphere was added geranyl bromide (2.17 g, 10 mmoles) in dry THF (15 mL) dropwise at -10°C. After stirring for 1hr, a catalytic amount of Li₂CuCl₄ (2 mL) was added to it. The resulting mixture was stirred for 3hr at -10°C and 12hr at room temperature and worked up as described for **1** to yield pure **2** (1.2g, 44%). R_f 0.695 in pet.ether; IR (neat) : 2940, 1650, 1260, 1110, 920, 820, 730 cm⁻¹; ¹H NMR: δ 0.9 (9H, 3×CH₃), 1.3 (s, 6H, 3×CH₂), 1.6 (d, 13H, J=9Hz, 3×CH₃-C=C,

Table I—Juvenile Hormone activity of juvenoids (**1-1e**, **2-2e**) on *Culex pipiens quinquefasciatus* Say

Compd	Doses in ppm	No. of larvae = 100				Activity index
		0	1	2	3	
1	10	0	4	24	72	2.68
	5	4	16	24	56	2.32
	2	15	22	37	24	1.68
	1	20	10	34	36	1.86
	0.5	44	4	36	16	1.24
1a	10	0	0	8	92	2.92
	5	0	3	5	92	2.89
	2	0	14	34	52	2.38
	1	11	23	30	36	1.91
	0.5	22	30	22	26	1.52
1b	10	0	0	3	97	2.97
	5	0	0	28	72	2.72
	2	0	5	32	63	2.58
	1	7	18	26	49	2.17
	0.5	20	16	28	36	1.8
1c	10	0	0	18	82	2.82
	5	0	11	53	36	2.25
	10	0	0	18	82	2.82
	5	0	11	53	36	2.25
	2	12	8	48	32	2.00
	1	20	16	38	26	1.70
	0.5	28	16	44	12	1.4
1d	10	0	5	31	64	2.59
	5	3	22	17	58	2.3
	2	13	15	28	44	2.03
	1	26	14	23	37	1.71
	0.5	46	4	20	30	1.34

Table I—Juvenile Hormone activity of juvenoids (**1-1e**, **2-2e**) on *Culex pipiens quinquefasciatus* Say (*Contd.*)

Compd	Doses in ppm	No. of larvae = 100				Activity index
		0	1	2	3	
1e	10	0	0	11	89	2.89
	5	0	0	18	82	2.82
	2	0	0	29	71	2.71
	1	0	8	44	48	2.40
	0.5	12	28	22	38	1.86
2	10	0	0	36	64	2.64
	5	4	16	40	40	2.16
	2	28	36	12	24	1.32
	1	32	32	20	16	1.2
	0.5	44	20	20	16	1.08
2a	10	0	24	12	64	2.4
	5	12	16	20	52	2.12
	2	21	24	24	14	1.44
	1	52	4	12	32	1.24
	0.5	72	4	8	16	0.68
2b	10	0	16	16	68	2.52
	5	12	8	24	56	2.24
	2	20	12	16	52	2.00
	1	36	16	12	36	1.48
	0.5	56	12	24	8	0.84
2c	10	0	12	24	64	2.52
	5	16	20	20	44	1.92
	2	28	0	24	48	1.92
	1	48	8	16	28	1.24
	0.5	64	12	8	16	0.76
2d	10	0	8	20	72	2.64
	5	16	0	36	48	2.16
	2	32	0	20	48	1.84
	1	48	0	28	24	1.28
	0.5	68	12	8	12	0.64
2e	10	0	8	28	64	2.56
	5	8	4	28	60	2.40
	2	16	8	20	56	2.16
	1	28	8	28	36	1.72
	0.5	48	20	16	16	1.00
M	5	0	0	0	100	3.00
	2	0	0	24	76	2.76
	1	0	3	49	48	2.45
	0.5	0	15	62	23	2.08

4×CH), 2.0 (s, 6H, 3×CH₂-C=C), 5.1 (bs, 2H, 2×CH=C); Anal. Calcd for C₂₀H₃₆: C, 86.87; H, 13.12. Found: C, 86.69; H, 13.0%.

1-(2-Pinen-10-yl)-3,7-dimethyl-6,7-epoxy-2(E)-octene 1a. To a well stirred ice-cold solution of **1** (0.272 g, 1 mmole) in dry CH₂Cl₂ (15 mL) was added

dropwise *m*-chloroperbenzoic acid (0.189 g, 1.1 mmole) in dry CH₂Cl₂ (10 mL) and stirred for 45 min at 0°C. After stirring for another 30 min at room temperature, it was decomposed with water, extracted with dichloromethane (3×20 mL) washed with 5% NaHCO₃ solution (20 mL), brine and dried.

Evaporation of solvent followed by column chromatography over neutral alumina using pet ether as eluent gave pure liquid **1a** (0.214g, 74.5 %). R_f 0.25 in pet.ether: ether (9.5 : 0.5); IR (neat) : 2940, 1640, 1210, 1120, 890, 800, 670 cm^{-1} ; ^1H NMR: δ 0.85(s, 3H, $\text{CH}_3\text{-C-CH}_3$), 1.2(s, 9H, $(\text{CH}_3)_2\text{-C-O-}$, $\text{CH}_3\text{-C-CH}_3$), 1.55(bs, 8H, $1\times\text{CH}_3\text{-C=C-}$, $2\times\text{CH}_2$, $1\times\text{CH}$), 1.86-2.55 (10H, $4\times\text{CH}_2\text{-C=C}$, $1\times\text{CH-C=C}$, O-CH), 5.1 (bs, 2H, $2\times\text{H-C=C}$); Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{O}$: C, 83.27; H, 11.18. Found : C, 83.15; H, 11.01%.

1-(2'-Isopropyl-5'-methylcyclohexyl)-3,7-dimethyl-6,7-epoxy-2(E)-octene 2a. Epoxidation of **2** (1.38 g, 5 mmoles) with *m*-chloroperbenzoic acid (0.948g, 5.5mmoles) in dry CH_2Cl_2 (50 mL) gave pure **2a** (1.18g, 81.4%). R_f 0.28 in pet ether : ether (9.5 : 0.5); IR (neat) : 2940, 1650, 1270, 1220, 1110, 810, 730, 680 cm^{-1} ; ^1H NMR (90 MHz): δ 0.8-0.9 (9H, $3\times\text{CH}_3$ of cyclohexyl group), 1.2 (d, 12H, $J=6\text{Hz}$, $3\times\text{CH}_2$ of cyclohexyl group, $2\times\text{CH}_3$), 1.6 (s, 9H, $1\times\text{CH}_2$, $1\times\text{CH}_3\text{-C=C}$, $4\times\text{CH}$ of cyclohexyl group), 1.95(s, 4H, $2\times\text{CH}_2\text{-C=C}$), 2.5(t, 1H, $J=12\text{Hz}$, OCH), 5.1(bs, 1H, HC=C); Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{O}$: C, 82.12; H, 12.40. Found: C, 82.05; H, 12.29 %.

1-(2'-Pinen-10-yl)-3,7-dimethyl-6,7-epithio-2(E)-octene 1b. A mixture of KSCN(0.194g, 2 mmoles), oxiran **1a** (0.576g, 2 mmoles), water (0.0198g, 1.1 mmoles) and ethanol(5mL) was stirred at room temperature for 24hr. The reaction mixture was filtered and residue was concentrated and then diluted with ether ($3\times 10\text{ mL}$) to precipitate the KOCN. It was filtered and the solvent evaporated to yield **1b** (0.43g, 71%). R_f 0.32 in pet ether : ethyl acetate (9.5:0.5); IR (neat) : 2920-2940, 1640, 1260, 1120, 890, 790 cm^{-1} ; ^1H NMR: δ 0.9 (s, 3H, $\text{CH}_3\text{-C-CH}_3$), 1.25 (s, 9H, $\text{CH}_3\text{-C-CH}_3$, $2\times\text{CH}_3$), 1.65 (s, 8H, $\text{CH}_3\text{-C=C}$, $2\times\text{CH}_2$, $1\times\text{CH}$), 2-2.5 (10H, $4\times\text{CH}_2\text{-C=C}$, $1\times\text{HC-C=C}$, SCH), 5.1 (bs, 2H, $2\times\text{CH=C}$); Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{S}$: C, 78.88; H, 10.59; S, 10.52. Found: C, 78.67; H, 10.46; S, 9.3%.

1-(2'-Isopropyl-5'-methylcyclohexyl)-3,7-dimethyl-6,7-epithio-2(E)-octene 2b. A mixture of **2a**(1.46g, 5 mmoles), KSCN(0.485 g, 5 mmoles) and water(0.054 g, 3 mmoles) in ethanol(20 mL) was stirred at room temperature for 24hr and worked up as usual to afford **2b** (1.14 g, 74%). R_f 0.37 in pet.ether : ethyl acetate (9:1); IR (neat): 2920, 1640, 1260, 1120, 1070, 910, 790, 680 cm^{-1} ; ^1H NMR: δ 0.9-1.0 (9H, $3\times\text{CH}_3\text{-C-}$ of cyclohexyl group), 1.3 (s, 12H, $3\times\text{CH}_2$

of cyclohexyl group, $(\text{CH}_3)_2\text{-CS}$), 1.63 (d, 9H, $J=9\text{Hz}$, $1\times\text{CH}_3\text{-C=C}$, $4\times\text{CH}$ of cyclohexyl group, SC-CH_2), 2.0-2.5 (5H, $2\times\text{CH}_2\text{-C=C}$, SCH-), 5.1 (bs, 1H, H-C=C); Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{S}$: C, 77.85; H, 11.76; S, 10.38. Found: C, 77.77; H, 11.61; S, 10.1%.

1-(2-Pinen-10-yl)-3,7-dimethyl-6,7-carbethoxymethylene-2(E)-octene 1c. To stirred mixture of **1** (2.72 g, 10 mmoles) and CuSO_4 (anhydrous) (0.747 g, 4.7 mmoles) at 90°C was added dropwise ethyl diazoacetate (1.72 g, 15 mmoles). Stirring was continued at this temperature for 2hr, cooled and diluted with ether, filtered and dried. Evaporation of the solvent followed by column chromatography of the residue over silica gel using pet ether ether (9:1) as eluent gave pure **1c** (1.18 g, 33 %). R_f 0.6 in pet.ether: ether (9:1); IR (neat): 2940, 1730, 1600, 1170, 780 cm^{-1} ; ^1H NMR : δ 0.9-1.3 (19H, $4\times\text{CH}_3$, $-\text{COOCH}_2\text{CH}_3$, $2\times\text{CH}_2$), 1.6 (5H, $\text{CH}_3\text{-C=C}$, $-\text{CHCCOOEt}$, $1\times\text{CH}$ of pinen ring), 1.9-2.3 (10H, $-\text{CHCCOOEt}$, $4\times\text{CH}_2\text{-C=C}$, $1\times\text{CH-C=C}$), 4.1(q, 2H, $J=33\text{Hz}$, $\text{COOCH}_2\text{CH}_3$), 5.1(s, 2H $2\times\text{CH=C}$); Anal. Calcd for $\text{C}_{22}\text{H}_{38}\text{O}_2$: C, 80.39; H, 10.68. Found: C, 80.26; H, 10.55 %.

1-(2'- Isopropyl-5'-methylcyclohexyl)-3,7-dimethyl-6,7-carbethoxymethylene-2(E)-octene 2c. A mixture of **2**(2.76 g, 10 mmoles) and anhydrous CuSO_4 (0.75 g, 4.7 mmoles) was treated with ethyl diazoacetate (1.72 g, 15 mmoles) at 90°C and worked up as usual to give **2c** (1.33g, 37%). R_f 0.41 in pet.ether: ethyl acetate (9:1); IR (neat) : 2920, 1720, 1640, 900, 810, 720, 700 cm^{-1} ; ^1H NMR : δ 0.9(s, 9H, $3\times\text{CH}_3$ of cyclohexyl group), 1.2(m, 17H, $4\times\text{CH}_2$, $2\times\text{CH}_3$, $\text{COOCH}_2\text{CH}_3$), 1.6(s, 8H, $1\times\text{CH}_3\text{-C=C}$, CHCCOOEt , $4\times\text{CH}$ of cyclohexyl group), 2.0-2.25 (5H, $2\times\text{CH}_2\text{-C=C}$, CHCCOOEt), 4.1(q, 2H, $J=33\text{Hz}$, $-\text{COOCH}_2\text{CH}_3$); 5.1(bs, 1H, CH=C); Anal Calcd for $\text{C}_{24}\text{H}_{42}\text{O}_2$: C, 79.49; H, 11.765. Found: C, 79.37; H, 11.56%

1-(2-Pinen-10-yl)- 3,7-dimethyl-2(3),6(7)-bisdi-chloromethyleneoctane 1d. A mixture of **1**(1.36 g, 5 mmoles) in chloroform(15 mL) and triethylbenzyl ammonium chloride (0.273 g, 1.2 mmoles) was stirred until the salt dissolved. To the resulting solution was added 50 % NaOH solution (5 mL) and stirring continued further for 3 days. The resulting mixture was diluted with water(10 mL), extracted with CHCl_3 and dried (CaCl_2). Solvent removal afforded **1d**(1.63 g, 79%). R_f 0.67 in pet. ether ethyl acetate (9.0 : 1.0);

IR (neat) : 2940, 1640, 1260, 1050, 920, 830-770 cm^{-1} ; ^1H NMR : δ 1-1.7 (26H, $5\times\text{CH}_3$, $4\times\text{CH}_2$, $3\times\text{CH}$), 2.2 (5H, $2\times\text{CH}_2\text{-C}=\text{C}$, $1\times\text{CH-C}=\text{C}$), 5.2 (s, 1H, $\text{CH}=\text{C}$); Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{Cl}_4$: C, 60.28; H, 7.36. Found : C, 60.15; H, 7.23%.

1-(2'-Isopropyl-5'-methylcyclohexyl)-3, 7-dimethyl-2(3), 6(7)-bisdichloromethyleneoctane 2d. Compound **2** (1.38 g, 5 mmol) was treated with CHCl_3 (22.1 g, 185 mmol) and 50 % NaOH solution (5 mL) in the presence of triethylbenzyl ammonium chloride (0.273 g, 1.2 mmol). Usual work up gave **2d** (1.76 g, 85%). R_f 0.68 in the pet. ether : ethyl acetate (9 : 1); IR (neat) : 2940, 1450, 1380, 830, 760 cm^{-1} ; ^1H NMR: δ 0.85-1.0 (d, 9H, $J=9\text{Hz}$, $3\times\text{CH}_3$ of cyclohexyl group), 1.2-1.8 (27H, $3\times\text{CH}_3$, $6\times\text{CH}_2$, $6\times\text{CH}$). Anal. Calcd for $\text{C}_{22}\text{H}_{36}\text{Cl}_4$: C, 59.73; H, 8.20. Found : C, 59.55; H, 8.11%.

1-(2-Pinen-10-yl)-3,7-dimethyl-2(3), 6(7)-bisdibromomethyleneoctane 1e. A solution of compound **1** (1.36 g, 5 mmol), bromoform (10 mL), 50% aq. NaOH (5 mL) in the presence of triethylbenzyl ammonium chloride (0.273 g, 1.2 mmol) was stirred for two days followed by usual work up to afford pure **1e** (2.26 g, 76.6 %). R_f 0.67 in pet ether : ethyl acetate (9:1); IR (neat) : 2940, 1680, 1040, 760-790, 660 cm^{-1} . ^1H NMR: δ 1.0-2.6 (31H, $5\times\text{CH}_3$, $4\times\text{CH}_2$, $2\times\text{CH}_2\text{-C}=\text{C}$, $1\times\text{CH-C}=\text{C}$, $3\times\text{CH}$), 5.2 (s, 1H, $\text{CH}=\text{C}$); Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{Br}_4$: C, 42.89; H, 5.23. Found : C, 42.75; H, 5.11 %.

1-(2'-Isopropyl- 5'-methylcyclohexyl)-3,7-dimethyl- 2(3),6(7)-bisdibromomethyleneoctane 2e. A mixture of **2** (1.38 g, 5 mmol), bromoform (46.8 g,

185 mmol) and 50 % aq. NaOH (5 mL) was stirred for three days in the presence of triethylbenzyl ammonium chloride (0.273 g, 1.2 mmol) to afford **2e** (2.53 g, 85.3 %). R_f 0.66 in pet. ether : ethyl acetate (9:1); IR (neat) : 2920, 1460, 1380, 750, 660 cm^{-1} ; ^1H NMR: δ 0.9 (d, 9H, $J=6\text{Hz}$, $3\times\text{CH}_3$ of cyclohexyl group), 1.1-1.8 (27H, $3\times\text{CH}_3$, $6\times\text{CH}_2$, $6\times\text{CH}$); Anal. Calcd for $\text{C}_{22}\text{H}_{36}\text{Br}_4$: C, 42.61; H, 5.85. Found : C, 42.46; H, 5.74%.

Acknowledgement

The authors express their sincere gratitude to the Science and Technology Council, Chandigarh Administration, Chandigarh for financial assistance.

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