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ISOLATION, TENTATIVE IDENTIFICATION, AND SYNTHESIS STUDIES OF THE VOLATILE COMPONENTS OF THE HAIRPENCIL SECRETION OF THE MONARCH BUTTERFLY

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Abstract—The major volatile components of the hairpencil secretion of the male monarch butterfly have been identified as benzyl caproate and either 1, 5, 5, 9-tetramethyl-10-oxabicyclo[4.4.0]-3-decen-2-one(**1**), or 2, 2, 6, 8-tetramethyl-7-oxabicyclo[4.4.0]-4-decen-3-one(**2**). One sequence designed to synthesize **1** yielded two isomeric products of structure **1** whose spectra are very similar to each other but distinctly different from those of the natural product; this sequence also yielded a tricyclic ketal (**9**). A second sequence gave two epimeric spiro compounds (**12**) and a third sequence gave a [4.3.0] ring system (**14**).

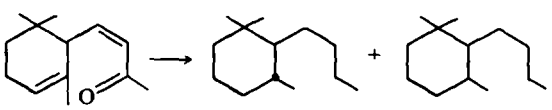
The wide-ranging migration habits and spectacular "roosting" sites—the "butterfly trees" of the California coast—make the monarch butterfly (*Danaus plexippus*) a fascinating subject for study[2] by lepidopterists, both professional and amateur. One of us (R.G.B.) had been involved for several years in a population study of the monarch butterfly in California,[3] and combined this avocation with the interests of our group in insect pheromones. During the summer of 1966 and 1967, we collected male monarchs, for this study, from roosting sites in eucalyptus trees on the California sites. The material was stored at −50°, and the work reported here was done in 1967–1968.

In common with many other male butterflies and moths, the male monarch butterfly possesses "hairpencils", which are extrusible brushlike organs whose function is to disperse pheromones during the pre-mating ritual. When we began this study of the monarch butterfly, Meinwald *et al.* had reported the identification of a pyrrolizidinone and two straight chain acetate esters from the hairpencils of another danaine, *Lycorea ceres ceres*.[4] Subsequently the same pyrrolizidinone and a terpenoid diol were identified from the hairpencils of the queen butterfly, *Danaus gilippus berenice*,[5] and the functions of these compounds and of the hairpencils were elucidated in three elegant studies.[6-8] Subsequently they have identified two compounds on thin layer chromatography of a methylene chloride extract of hairpencils of the male monarch: *trans, trans*-3, 7 - dimethyl - 2, 6 - decadien - 1, 10 - dioic acid, and *trans, trans* - 10 - hydroxy - 3, 7 - dimethyl - 2, 6 - decadienoic acid.[9,10]

We have identified two compounds, an ester and a ketone, by GLC of a benzene extract of the distillate obtained by subjecting macerated abdominal tips directly to short path, high vacuum distillation. Although the hairpencils had a distinct floral odor, attempts to isolate an odorous compound failed. The two compounds identified accounted for the only major GLC peaks present and for more than 90% of all the peak areas. Since no bioassays have been carried out on any of the compounds isolated, they cannot be properly described as pheromones, and their functions remain unknown. The same GLC peaks were obtained from an extract of hairpencil hairs (cut with a razor blade against a Teflon block) from 22 live males.

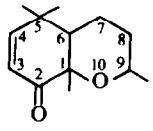
The ester was quickly identified as benzyl caproate, and this was confirmed by matching the mass, IR, NMR and UV spectra with those of an authentic sample.

The molecular formula of the ketone was $C_{13}H_{20}O_2$, requiring four sites of unsaturation. The IR, NMR, and UV spectra suggested that the compound was a bicyclic α,β-unsaturated ketone with an ether oxygen forming one ring. Optical activity was not determined because of the small amount of material. The conspicuous features of the NMR spectrum were four Me groups and two olefinic protons. Hydrogenolysis[11] yielded two compounds with very similar mass spectra (M 182); the same compounds (matched retention times and mass spectra) were obtained on hydrogenolysis of α-ionone:

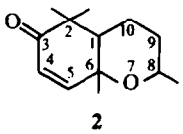


α-ionone M 182 M 182

On this evidence, we proposed one or the other of the following structures. Nothing could be said about the stereochemistry. Compound **1** is 1, 5, 5, 9 - tetramethyl - 10 - oxabicyclo[4.4.0] - 3 - decen - 2 - one. Compound **2** is 2, 2, 6, 8 - tetramethyl - 7 - oxabicyclo[4.4.0] - 4 - decen - 3 - one. This terpenoid oxabicyclo [4.4.0] ring system has recently been described; the "rose compounds" from purple passionflower juice have the same skeleton, but lack the ketone function.[12]



1

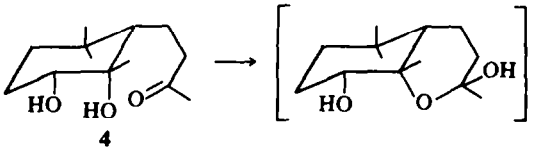


2

We now describe three sequences designed to synthesize **1**.

The first sequence gave two isomeric products of structure **1**, whose spectra were very similar to each other but distinctly different from those of the natural product: α-Ionone was hydrogenated over Raney nickel with one mole of hydrogen at one atmosphere. The dihydro-ionone (**3**) was treated with osmium tetroxide in tetrahydrofuran-pyridine at room temperature for 70 hours, then with hydrogen sulfide. The dihydroxy-compound (**4**) was ring-closed on distillation at 130–150°/20 mm to give the unsaturated cyclic hydroxy ether (**5**) as the major product, which gave the saturated cyclic hydroxy ether (**6**) on hydrogenation over platinum oxide, and the corresponding ketone (**7**) on oxidation of **6** with Jones reagent. Bromination with trimethylphenylammonium tribromide in tetrahydrofuran gave **8**, which on dehydrobromination with lithium bromide and lithium carbonate in dimethylformamide gave the two isomeric α, β-unsaturated ketones of structure **1**, which are probably epimeric at C_9.

A minor product from the ring-closure reaction was identified as a tricyclic structure **9**, presumably resulting from ketalization of any of the *cis*-fused compound formed. This suggests that the two epimers of structure **1** may be *trans*-fused.



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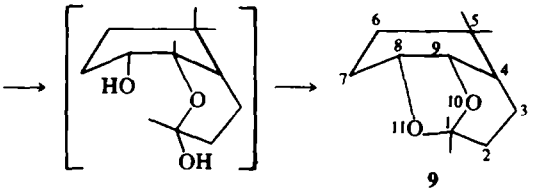

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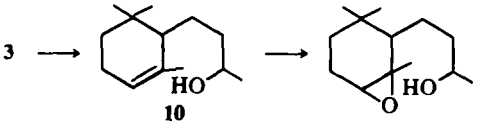
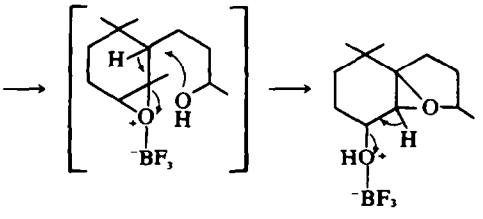
The second approach to structure **1**, which involved sequential treatment of dihydro-α-ionone (**3**) with LAH, *m*-chloroperbenzoic acid, and boron trifluoride etherate, gave two unexpected, though rational, epimeric products of structure **12** by way of the unsaturated alcohol (**10**) and the alcohol epoxide (**11**). This sequence followed by allylic oxidation should provide a synthesis of theaspirone, one of the components of tea aroma.[13]



10 **11**



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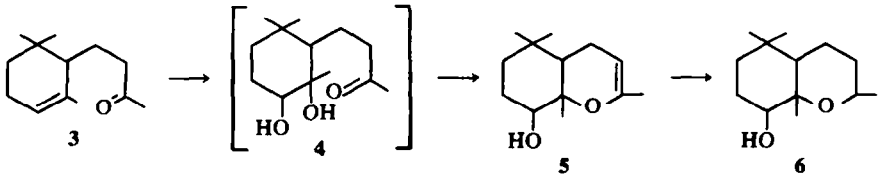
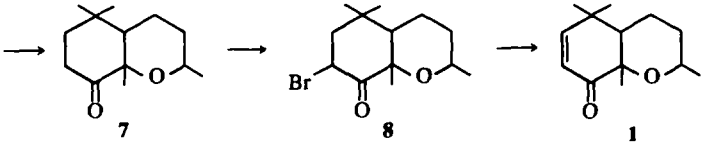
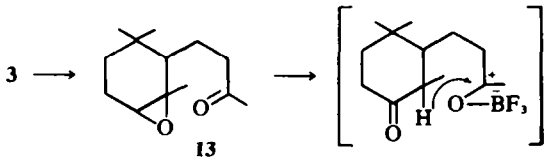


3 **4** **5** **6**



7 **8** **1**

A third approach to structure 1, which involved treatment with boron trifluoride etherate of the epoxide (13) obtained from dihydro-α-ionone (3), resulted in the [4.3.0] structure (14), presumably by way of rearrangement of the epoxide group to a ketone.



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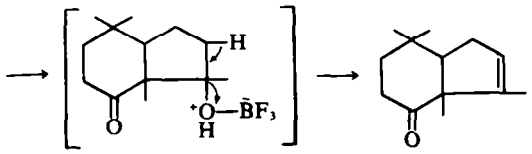

14

Synthetic approaches to structure 2 are under investigation.

EXPERIMENTAL

Isolation and identification. Frozen abdominal tips from 1250 male Monarch butterflies were ground and subjected to short-path, high-vacuum distillation (110–120°/0·05 mm Hg for 100 min) onto a condenser cooled with Dry-ice/acetone. Additional distillate was obtained by extracting the residue in a blender with benzene, concentration and redistilling. The distillate, in benzene, was fractionated by GLC (4% SE 30 on Chromosorb G 60/80 mesh, 1·5 m × 4 mm glass, 25 cm³ He/min, 70–170° at 4°/min, ketone retention 26 min, 670 μg, ester retention 28·5 min, 850 μg. Each collected compound was homogeneous on a QF1 column (2% on Chromosorb W 60/80 mesh, 1·5 m × 2 mm glass, 25 cm³ He/min, 50–200° at 6° min, ester retention 10 min, ketone retention 10·5 min).

The following major peaks were present in the mass spectrum of the isolated ketone: (% of base, formula by high resolution): 208 (M, 8%, $C_{13}H_{20}O_2$), 193 (11%), 165 (5%, $C_{10}H_{13}O_2$), 98 (67%, $C_5H_6O_2$), 69 (base, C_5H_9 and C_4H_5O), 55 (35%), 43 (58%), 41 (65%). The IR spectrum (μm, CCl_4) showed a C=O peak at 5·92 (shoulder at 6·02) a weak C=C peak at 6·20, a moderate peak at 8·05, strong peaks at 8·95, 9·25, and 9·35 m presumably due to the ether group. The UV absorption was at 219 nm (ε 15,000). The NMR spectrum was (τ, 100 MHz, CCl_4): 8·90, 8·70 (each 3 protons, each s, CH_3 groups on C_5), 8·86 (3 protons, d, J ~ 6Hz, upper peak under peak at 8·90), 8·45 (3 protons, s, CH_3 on C_1) 6·60 (1 proton, m, C_9), 4·27 (1 proton, d, J ~ 10 Hz, C_3), 3·58 (1 proton, d, J ~ 10 Hz, C_4). The numbering is that given for structure 1.

Synthesis

1, 5, 5, 9 - *Tetramethyl* - 10 - *oxabicyclo* [4.4.0] - 8 - *decen* - 2 - *ol*(5) *and* 1, 5, 5, 9 - *tetramethyl* - 10, 11 - *dioxatricyclo* [6.2.1.0^{4,9}] *undecane* (9). A soln of dihydro-α-ionone 3 (from Raney nickel hydrogenation of α-ionone that had been purified by gas liquid chromatography) (750 mg; 38 mmoles), osmium tetroxide (1·0 g; 5·3 mmoles), pyridine (0·61 g), and THF (20 ml) was allowed to stand at room temp for 70 h, treated with H_2S and filtered and washed with THF (Caution! the ppt is pyrophoric when dry). The soln was diluted with ether and hexane, washed twice with saturated brine, and dried over $MgSO_4$. Solvent removal *in vacuo* gave a brown oil whose IR spectrum showed strong CO and OH bands.

Tube-distillation at 130–150°/20 mm gave 645 mg of a liquid, which showed three major components on GLC analysis with retention times of 1·6, 2·6, and 3·8 min (area ratios 1·4 : 10 : 76); the 2·6 min component was dihydro-α-ionol (5% Carbowax 20M on Chromosorb W, HMDS, 60/80 mesh, 5′ × 1/8″ aluminum, 142°, 25 cm³ He/min).

Compound 5 (retention 17·0 min) and Compound 9 (retention 7·8 min) were isolated by preparative GLC (4% Carbowax 20 M on Chromosorb W, HMDS, 60/80 mesh, 5′ × 1/4″ aluminum, 145°, 30 cm³ He/min). Dihydro-α-ionone had a retention time of 11·2 min.

Compound 5: NMR (τ, 60 MHz, CCl_4): 5·59 (1H, m, $w_{1/2}$ 10 Hz, C_6), 6·38 (1H, m, $w_{1/2}$ 7 Hz, C_2), 7·63 (1H, s, OH), 8·13 (3H, m, $w_{1/2}$ 5Hz, CH_3 on C_9), 8·85 (3H, s, CH_3 on C_1) 9·04, 9·15 (each 3H, each s, CH_3 groups on C_5). IR (film, μm) 3·0(OH), 5·95 (C=C). (Found: C, 74·36; H, 10·61. Calc. for $C_{13}H_{22}O_2$: C, 74·24; H, 10·54%).

Compound 9: NMR (τ, 60 MHz, CCl_4) 6·55 (1H, t, C_6), 8·61 (3H, s, CH_3 on C_1), 8·67 (3H, s, CH_3 on C_9), 9·00, 9·05 (each 3H, each s, CH_3 groups on C_5). Mass: M 210. (Found: C, 74·48; H, 10·71. Calc. for $C_{13}H_{22}O_2$: C, 74·24; H, 10·54%).

1, 5, 5, 9 - *Tetramethyl* - 10 - *oxabicyclo*[4.4.0] - 2 - *decanol* (6). A mixture of 5 (180 mg, 0·85 mmole), PtO_2 (40 mg), and 72% perchloric acid (60 mg) was stirred in a H_2 atmosphere until a molar equiv of H_2 was absorbed. The mixture was neutralized with solid $NaHCO_3$ and filtered, and the solvent was removed *in vacuo*. The major product (ratio of epimers 9 : 1) was isolated by GLC (8% Carbowax 20 M on Chromosorb G 60/80 mesh, 6′ × 1/4″ aluminum, 160°, 80 cm³ He/min, 30 cm³ while collecting, retention 14·0 min). NMR (τ, 100 MHz, CCl_4): 6·29 (1H, m, C_9) 6·61 (1H, m, $w_{1/2}$ 6 Hz, C_2), 8·85 (3H, s, CH_3 on C_1), 8·95 3H, d, J ~ 6 Hz, CH_3 on C_9), 9·14 and 9·28 (each 3H, each s, CH_3 groups on C_5). (Found: C, 73·57; H, 11·45. Calc. for $C_{13}H_{24}O_2$: C, 73·54; H, 11·39%).

1, 5, 5, 9 - *Tetramethyl* - 10 - *oxabicyclo*[4.4.0] - 2 - *decanone* (7). A stirred soln of 6 (80 mg including the minor epimer, 0·38 mmole) in 25 ml acetone was titrated with Jones reagent, and the mixture was diluted with ether, washed with saturated brine, and dried over Na_2SO_4 ($MgSO_4$ removed the ketone, presumably by chelation). The oil (used in next step) that remained on solvent removal showed two compounds (presumably isomers) in a 1 : 9 ratio (5% Carbowax 20 M on Chromosorb W HMDS 60/80 mesh, 5′ × 1/8″ aluminium, 170°, 28 cm³ He/min, retention of minor component 7·8 min, of major component 8·7 min). The major component was isolated by GLC (8% Carbowax 20 M on Chromosorb G 60/80 mesh, 6′ × 1/4″ aluminum) 200°, 100 cm³ He/min, 30 cm³ while collecting, retention 15 min, that of minor component 13 min). IR (μm, CCl_4): 5·76 (C=O), NMR (τ, 100 MHz, CCl_4): 6·35 (1H, m, C_9), 7·66 (2H, m, C_3), 8·65 (3H, s, CH_3 on C_1), 8·87 (3H, d, J ~ 6 Hz, CH_3 on C_9), 9·03, 9·04 (each 3H, each s, CH_3 groups on C_5). (Found: C, 74·19; H, 10·50. Calc. for $C_{13}H_{22}O_2$: C, 74·24; H, 10·54%).

3 - *Bromo* - 1, 5, 5, 9 - *tetramethyl* - 10 - *oxabicyclo*[4.4.0] - 2 - *decanone* (8). The oily residue (57 mg; 0·27 mmole) from solvent removal in the previous step was dissolved in 5 ml THF and treated with 107 mg (0·27 mmole) trimethylphenylammonium tribromide.

After 10 min, acetone was added to remove any excess reagent, and the mixture was poured into water and extracted with hexane. The hexane soln was dried with Na_2SO_4. On solvent removal, a crystalline residue (used in next step) remained, from which an analytical sample was obtained by recrystallization from ether on cooling with Dry-ice, m.p. 145–147·5°; IR (μm, CCl_4): 5·72 (C=O); NMR (τ, 100 MHz, CCl_4): 5·12 (1H, dd, J 13·3 and 6·2 Hz, C_3 axial), 6·30 (1H, m, C_9), 8·56 (3H, s, CH_3 on C_1), 8·34 (3H, d, J ~ 6 Hz, CH_3 on C_9), 8·96 and 9·00 (each 3H, each s, CH_3 groups on C_5). (Found: C, 54·85; H, 7·60. Calc. for $C_{13}H_{21}BrO_2$: C, 53·99; H, 7·32%).

1, 5, 5, 9 - *Tetramethyl* - 10 - *oxabicyclo*[4.4.0] - 3 - *decen* - 2 - *one* (**1**). A soln of crude **8** (50 mg; 0·20 mmole), Li_2CO_3 (100 mg) and anhyd LiBr[14] (90 mg) was heated at 150–160° for 1 h. The cooled mixture was poured into water. Extraction with hexane, washing four times with brine, drying over Na_2SO_4, and solvent removal left an oil that showed two products on GLC in a 1:9 ratio (5% Carbowax 20M on Chromosorb W HMDS 60/80 mesh, 5′ × 1/8″ aluminum, 170°, 25 cm³ He/min, retentions 7·8 and 9·1 respectively. The major isomer (30 mg) was isolated by GLC (8% Carbowax 20 M on Chromosorb G 60/80 mesh, 6′ × 1/4″ aluminium, 200°, 100 cm³ He/min, 34 cm³ He/min while collecting, m.p. (crystallized on standing) 66–69°. The mass spectrum showed (% of base): 208 (M, 3%), 193 (2%), 165 (2%), 112 (60%), 96 (base), 71 (21%), 69 (14%), 55 (22%), 43 (60%), 41 (40%); IR (μm, CCl_4): 5·87 (C=O, shoulder at 6·02), 6·20 (C=C, stronger than that in isolated 1, 8·05 (mod), 8·90, 9·05, 9·35 (strong, presumably C–O–C); NMR (τ, 60 MHz, CCl_4): 3·65 (1H, d, J 10·3 Hz, C_4), 4·30 (1H, d, J 10·3 Hz, C_3), 6·28 (1H, m, C_9), 8·66 (3H, s, CH_3 on C_1), 8·82 (3H, d, J 6 Hz, upper peak under peak at 8·86, CH_3 on C_9), 8·86 and 8·96 (each 3H, each s, CH_3 groups on C_5. (Found: C, 75·37; H, 10·05, Calc. for $C_{13}H_{20}O_2$: C, 74·96; H, 9·68%).

The minor isomer (2 mg) was isolated by GLC (same conditions). Mass spectrum (% of base peak): 208 (M, 4%), 193 (2%), 165 (3%), 112 (62%), 96 (base), 71 (18%), 69 (9%), 55 (10%), 43 (42%), 41 (18%); IR (μm, CCl_4): 5·87 (C=O, shoulder at 6·02) 6·20 (C=C, wk), 8·75, 8·90, 9·10, 9·35 (strong, C–O–C); NMR (τ, 100 MHz, CCl_4): 3·74 (1H, d, J 10·0 Hz, C_4) 4·35 (1H, d, J 10 Hz, C_3), 6·10 (1H, m, C_9), 8·75 (3H, s, CH_3 on C_1), 8·82 (3H, d, J 6 Hz, CH_3 on C_9), 8·88 and 8·92 (each 3H, each s, CH_3 groups on C_5).

Dihydro-α-ionol (**10**). A mixture of **3** (1 g; 5·1 mmoles) and LAH (0·19 g; 4·8 mmoles) in 60 ml ether was held at room temp. After 20 min, a saturated soln of $MgSO_4$ was added dropwise, followed by anhyd $MgSO_4$, and the ether soln was decanted. The solids were washed twice with ether, and the combined ether solns were concentrated *in vacuo* to an oily residue; NMR (τ, 60 MHz, CCl_4): 4·73 (1H, m, olefinic), 6·37 (1H, m, CHOH), 8·30 (3H, m, CH_3 on olefin), 8·85 (3H, d, J 7 Hz, CH_3CHOH), 9·06 and 9·11 (each 3H, each s, gem dimethyl).

Dihydro-α-ionol epoxide (**11**). A soln of **10** (325 mg; 1·65 mmoles) and m-chloroperbenzoic acid (500 mg; 2·89 mmoles) in 25 ml benzene was held at room temp for 2 h and poured into water. The benzene soln was washed with dil $NaHCO_3$ aq, dil $NaHSO_3$ aq, dil $NaHCO_3$ aq (2X), and water (2X); the soln was dried over $MgSO_4$ and the solvent was removed to leave an oily residue; NMR (τ, 60 MHz, CCl_4): 6·28 (1H, m, $w_{1/2}$ 20 Hz, CHOH), 7·13 (1H, m, $w_{1/2}$ 5 Hz, epoxide proton), 8·70 (3H, s, CH_3 on epoxide), 8·81 (3H, d, J 6 Hz, CH_3CHOH), 9·13, 9·18 (each 3H, each s, gem CH_3 groups).

Spiro[4.5] - 2, 6, 10, 10 - *tetramethyl* - 1 - *oxa* - 6 - *decene* (**12**). A soln of (150 mg; 0·71 mmole) (**11**) and 6 drops BF_3-etherate in 6 ml ether was held at room temp for 100 min, and a dil $NaHCO_3$ aq was added. The ether soln was washed with water, dried over $MgSO_4$, and the solvent was removed. The oily residue was subjected to GLC (8% Carbowax 20 M on Chromosorb G 60/80 mesh, 6′ × 1/4″ aluminum, 120°, 80 cm³ He/min, 30 cm³ while collecting fraction from 6–10 min. This fraction was reinjected on the same column at 118°, 23 cm³ He/min and two fractions were collected with retention times of 24 and 29 min respectively. The molecular formula by high resolution mass spectrometry for both samples was $C_{13}H_{22}O_2$. Each spectrum showed a major peak at *m/e* 138, representing loss of $(CH_3)_2CCH_2$. The 24 min compound showed the following NMR spectrum (τ, 100 MHz, CCl_4): 4·86 (1H, m, $w_{1/2}$ 10 Hz, C_7), 6·00 (1H, m, C_2), 8·35 (3H, s with long-range coupling, CH_3 on C_6), 8·88 (3H, d, J 5·5 Hz, CH_3 on C_2), 9·13 and 9·17 (each 3H, each s, CH_3 groups on C_{10}). The 29 min compound showed the following NMR spectrum (τ, 100 MHz, CCl_4): 4·77 (1H, m, $w_{1/2}$ 10 Hz, C_7), 6·03 (1H, m, C_2), 8·38 (3H, s with long-range coupling, CH_3 on C_6), 8·81 (3H, d, J 5·9 Hz, CH_3 on C_2), 9·09 and 9·17 (each 3H, each s, CH_3 groups on C_{10}).

Dihydro-α-ionone epoxide (**13**). A soln of **3** (1·0 g; 5·1 mmoles) and m-chloroperbenzoic acid (1·3 g; 7·5 mmoles) in 25 ml benzene was allowed to stand at room temp for 2 hr and poured into water. The benzene soln was washed with dil $NaHSO_3$ aq, dil Na_2CO_3 aq, and water. Removal of the solvent left an oil that was subjected to GLC (20%, Carbowax 20 M on Chromosorb W 45/60 mesh, 6′ × 3/8″ aluminum, 155°, 100 cm³ He/min, 25 cm³ during collection between 30 and 40 min; NMR (τ, 60 MHz, CCl_4): 7·20 (1H, m, epoxide H), 7·5 (2H, m, CH_2C=O), 7·92 (3H, s, CH_3–C=O), 8·73 (3H, s, CH_3 on epoxide), 9·10 and 9·14 (each 3H, each s, gem CH_3 groups).

1, 5, 5, 9 - *Tetramethyl* - *bicyclo*[4.3.0] - 8 - *nonen* - 2 - *one* (**14**). A mixture of **13** (63 mg; 0·29 mmoles) and BF_3-etherate (80 mg) in 3 ml hexane was allowed to stand at room temp for 1 hr and poured into dil $NaHCO_3$ aq. The hexane soln was washed with water, dried over $MgSO_4$, and the solvent was removed. Purification required two sequential passages through GLC. The material was collected as a broad peak on 4% SE 30 on Chromosorb G 45/60 mesh, 6′ × 1/4″, 48 cm³ He/min. GLC on an analytical column (5% Carbowax 20M on Chromosorb W HMDS 60/80 mesh, 5′ × 1/8″, 127°, 20 cm³ He/min) showed a major component at a retention of 6·3 min and a minor at 4·6 min (ratio 5:1). The major component was isolated on 8% Carbowax 20 M on Chromosorb G 60/80 mesh, 6′ × 1/4″ aluminium, 180°, 100 cm³ He/min, 30 cm³/min while collecting. Mass spectrum: M 192. IR (μm, CCl_4) 5·85 (C=O); NMR (τ, 100 MHz, CCl_4): 4·64 (1H, m, $w_{1/2}$ 6 Hz, C_8), 8·50 (3H, s with long-range coupling, CH_3 on C_9), 8·82 (3H, s, CH_3 on C_1), 9·01 and 9·09 (each 3H, each s, CH_3 groups on C_5).

REFERENCES

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[2] F. A. Urquhart, *The Monarch Butterfly* University of Toronto Press (1960)

[3] F. A. Urquhart, P. Beard and R. Brownlee, *J. Research on the Lepidoptera* 4 (4), 221 (1965)

[4] J. Meinwald, Y. C. Meinwald, J. W. Wheeler, T. Eisner

and L. P. Brower, *Science* **151**, 683 (1966); J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.* **88**, 1305 (1966)
[5]J. Meinwald, Y. C. Meinwald and P. H. Mazzochi, *Science* **164**, 1174 (1969)
[6]T. E. Pliske and T. Eisner, *Ibid.* **164**, 1170 (1969)
[7]*D. Schneider and U. Seibt, Ibid.* **164**, 1173 (1969)
[8]J. Myers and L. P. Brower, *J. Insect Physiol.* **15**, 2117 (1969)
[9]J. Meinwald, A. M. Chalmers, T. E. Pliske and T. Eisner, *Chem. Comm.* **86** (1969)
[10]J. Meinwald, A. M. Chalmers, T. E. Pliske and T. Eisner, *Tetrahedron Letters*, 4893 (1968)
[11]M. Beroza and B. A. Bierl, *Analyt. Chem.* **39**, 1131 (1967). R. G. Brownlee and R. M. Silverstein, *Ibid.* **40**, 2077 (1968)
[12]F. B. Whitfield, G. Stanley and K. E. Murray, *Tetrahedron Letters* 95 (1973)
[13]K. Ina, Y. Sakato and H. Fukami, *Ibid.* 2777 (1968)
[14]R. Joly and J. Warrant, *Bull. Soc.* 366 (1958)