$a_i(s) + b_i(p_i) \equiv sp^n$, $n = (b_i/a_i)^2$, which maximize the sum

$$S = k_{CH}\sum S_{CH} + k_{CC}\sum S_{CC} \qquad (1)$$

where S_{CH} and S_{CC} are overlaps of C–H and C–C bonds, respectively. The weighting factors $k_{CH} = 135.86$ and $k_{CC} = 121.17$ take into account the fact that the same overlap in different bonds corresponds to different bond energies. The coefficients a_i, b_i, are subject to the orthogonality relationship: $a_ia_j + b_ib_j \cos \theta_{ij} = \delta_{ij}$, where θ_{ij} is angle between the directions of hybrids ψ_i and ψ_j centered at the same atom. By systematic variation of independent parameters for an assumed initial hybrid composition the maximum bond overlaps and the best hybridizations were found. For atomic functions, those suggested by Clementi[18] have been adopted, assuming the experimental bond lengths. The necessary basic overlap integrals are taken from the available tables.[19] During the calculations the bond angles were allowed to follow the directions of hybrids freely, except in cyclic systems where necessarily bent bonds appear. The calculated C–C bond overlaps, experimental C–C bond lengths, and the corresponding maximum overlap hybrids associated with the bond for a selection of molecules are listed in Table I. The following linear relationship between C–C bond lengths and bond overlap is found.

Table I. Calculated C–C Bond Overlaps and Bond Lengths According to the Maximum Overlap Approximation

Molecule	Overlap	Exptl bond length, Å	Hybrids	Calcd bond length, Å
Diacetylene	0.7889	1.379	$sp^{1.15}$–$sp^{1.15}$	1.378
Vinylacetylene	0.7370	1.448	$sp^{1.20}$–$sp^{2.23}$	1.439
Methylacetylene	0.7184	1.459	$sp^{1.18}$–$sp^{3.01}$	1.460
Cyclooctatetraene	0.7139	1.462	$sp^{2.10}$–$sp^{2.10}$	1.466
1,3-Butadiene	0.7062	1.483	$sp^{2.23}$–$sp^{2.23}$	1.475
Diphenyl	0.7015	1.492	$sp^{2.19}$–$sp^{2.19}$	1.480
Propylene	0.6847	1.501	$sp^{2.18}$–$sp^{3.01}$	1.500
Isobutylene	0.6775	1.507	$sp^{2.22}$–$sp^{3.22}$	1.508
Isobutane	0.6566	1.525	$sp^{3.00}$–$sp^{3.15}$	1.532
Neopentane	0.6514	1.540	$sp^{3.00}$–$sp^{3.22}$	1.538
Ethane	0.6476	1.543	$sp^{3.20}$–$sp^{3.20}$	1.543

$$\text{C–C (Å)} = -1.166S_{CC} + 2.298 \qquad (2)$$

This relationship is used to reproduce the bond lengths in the last column of Table I. A similar relationship was found for C–H bond lengths.

$$\text{C–H (Å)} = -0.869S_{CH} + 1.726 \qquad (3)$$

A selection of molecules on which the evaluation of the above linear relationship between C–H bond overlap and bond length was based together with the corresponding values of C–H bond overlaps, experimental C–H bond lengths used, and the maximum overlap hybrids found are listed in Table II. The last column gives the calculated bond lengths. The bond length–bond overlap correlations can be used in an iterative procedure and applied to systems for which the variations in C–C bonds are not known. One starts by assuming a standard value for C–C and C–H bond lengths. Then by calculating the maximum overlap hybrids the new bond lengths are deduced from the corresponding bond overlaps, and the process is repeated until the input and the output bond lengths are equal. For example, if we assume deliberately long C–C and C–H bond lengths in diacetylene (1.54 and 1.08 Å, respectively) after eight iterative steps they are reduced to the expected values: 1.38 Å for an sp–sp single C–C bond and 1.065 Å for an sp C–H bond. This is in full agreement with the experimental values of Craine and Thompson,[20] not used in obtaining the correlations. The convergence could be considerably improved if one starts with bond lengths which are close to the values corresponding to various sp^n–sp^m (n, m = 1, 2, 3) types.

Table II. Calculated C–H Bond Overlaps and Bond Lengths According to the Maximum Overlap Approximation

Molecule	Overlap	Exptl bond length, Å	Hybrids	Calcd bond length, Å
Acetylene	0.7686	1.059	$sp^{1.30}$	1.058
Benzene	0.7412	1.084	$sp^{2.18}$	1.082
Ethylene	0.7403	1.085	$sp^{2.17}$	1.083
Cyclopropane	0.7328	1.089	$sp^{2.50}$	1.089
Cyclooctatetraene	0.7356	1.090	$sp^{2.32}$	1.087
Cyclobutane	0.7287	1.092	$sp^{2.65}$	1.093
Ethane	0.7196	1.102	$sp^{2.94}$	1.101

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[18] E. Clementi, *IBM J. Res. Develop. Suppl.*, **9**, 2 (1965).

[19] L. Klasinc, D. Schulte-Frohlinde, and M. Randić, *Croat. Chem. Acta*, **39**, 125 (1967).

[20] G. D. Craine and H. W. Thompson, *Trans. Faraday Soc.*, **49**, 1273 (1953).

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Received December 15, 1969

Synthetic Studies on Insect Hormones. IX.[1,2] Stereoselective Total Synthesis of a Racemic Boll Weevil Pheromone

Sir:

Recent isolation[3] of the sex attractant of the male boll weevil (*Anthonomus grandis* Boheman) followed a most difficult phase of insect pheromone research[4] and allowed structure elucidation[4] of the essential components as the monoterpenes **1**, **2**, and **3** or **4**, which have recently been synthesized by nonselective routes.[5]

We wish to report the first stereoselective synthesis of racemic **1** which now defines unambiguously the stereochemistry of the natural product and provides a practical route to material for experimental evaluation in insect control.

Since the stereochemistry of the pheromone **1** was unknown at the outset, it was planned to derive the iso-

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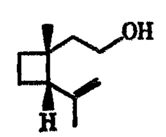
[1] Part VIII: see J. B. Siddall, M. Biskup, and J. H. Fried, *J. Amer. Chem. Soc.*, **91**, 1853 (1969).

[2] Contribution No. 1 from the Research Laboratory of Zoëcon Corporation.

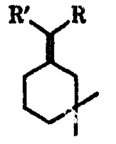
[3] Announced at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13–18, 1969. See also ref 5.

[4] *Chem. Eng. News*, **47** (18), 36 (1969).

[5] Completion of a nonselective synthesis of **1** and its *trans* isomer was announced on Sept 10, 1969 at the 158th National Meeting of the American Chemical Society, New York, N. Y., by J. H. Tumlinson, D. D. Hardee, R. C. Gueldner, A. C. Thompson, P. A. Hedin, and J. P. Minyard, *Science*, **166**, 1010 (1969).



1

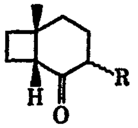


2, R = CH$_2$OH; R′ = H
3, R = CHO; R′ = H
4, R = H; R′ = CHO

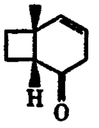
propenyl group by Wittig methylenation of an acetyl group which could allow access by stereochemical inversion from the *cis* to *trans* series. With the expectation that a deliberately allowed equilibration of the *cis*-related bulkier side chains in **10** might favor the less crowded *trans* form, the safer initial aim was seen to be stereospecific synthesis of the *cis* isomer.

By careful oxidative disconnection of a suitable *cis*-fused bicyclo[4.2.0]octane derivative **9**, both the required acetyl group and the necessary *cis* relationship of side chains are ensured.

Synthesis of *cis*-2,6-dimethylbicyclo[4.2.0]oct-3-en-2-ol (**9**) commenced by photochemical cycloaddition of ethylene to 3-methylcyclohex-2-enone to give, in 55% yield, *cis*-6-methylbicyclo[4.2.0]octan-2-one[6a] (**5**) which was brominated in 85% yield with 1.1 equiv of phenyltrimethylammonium tribromide[6b] in tetrahydrofuran at 20°. Observation of two methyl singlets at 1.26 and 1.35 in the nmr spectrum[7] of the bromoketones **6** indicated a 3:1 mixture of isomers which was dehydrobrominated with lithium carbonate in dimethylacetamide at 125°. Gas chromatographic (gc) analysis[8a] showed the product to contain 16% oft he β,γ-unsaturated ketone[9] **7**: bp bath 45° (12 mm); ir (CCl$_4$) 1710 cm^{-1}; nmr 1.23 (s, CH_3) and 5.66 (broad s, 4 and 5-H) together with 73% of the required conjugated ketone[10] **8**: bp 45–47° (0.45 mm); uv max (cyclohexane) 223 (ϵ 7950) and 280 nm (ϵ 74); ir (CCl$_4$) 1670 cm^{-1}; nmr 1.33 (s, 6-CH_3), 6.12 (two t, $J_{3,4}$ = 10.5, $J_{3,5}$ = 2, 3-H), and 6.88 (two t, $J_{4,5}$ = 4, 4-H). Aqueous methanolic sodium carbonate treatment of **7** led to a 64:36 equilibrium ratio in favor of **8**.



5, R = H
6, R = Br



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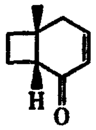
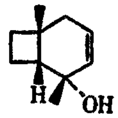


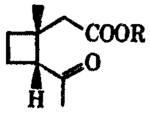
8

The methyl of the envisioned acetyl group was introduced by ethereal methyllithium alkylation of **8** to give in quantitative yield a single isomer of a crystalline alcohol[10] **9**: mp 60–61°; ir (CCl$_4$) 3600 cm^{-1}; nmr 1.1[illegible], 1.19 (two s, 2-CH_3 and 6-CH_3), and 5.84 (m, half-width 4 Hz, 3-H and 4-H).

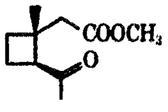
Ring opening of the *cis*-olefinic alcohol **9**, carried out by osmium tetroxide catalyzed sodium periodate oxidation[11] at 20° for 15 hr in ether–water (1:1), was sufficiently mild to afford a single *cis*-keto acid **10**:[10] bp 58–60° bath (0.05 mm); ir (CCl$_4$) 3515 (free OH), 3400–2500, and 1708 cm^{-1}; nmr 1.41 (s, 1-CH_3), 2.11 (s, COCH_3), 2.51 (s, CH_2COOH), 3.09 (t, J = 7, 2-H), and 9.40 (COOH), isolated in 51% yield after short-path distillation. Gc analysis[8b] of the derived methyl ester **11** showed that less than 1% of the *trans*-isomer **12** was present, since a 1-hr exposure of **11** to the basic resin IRA-400[12] in methanol enhanced the *trans*-isomer peak to 64% and led after 19 hr to an equilibrium mixture of 29.5:70.5 in favor of **12**. The nmr spectrum of **11** showed a singlet methyl at 1.39 and an adjacent methylene singlet at 2.47 in contrast to 1.10 (s, CH_3) and 2.57 (s, CH_2) for the *trans*-isomer[8c] **12**, but proof of *cis* stereochemistry of **11** came from rapid lithium tri-*t*-butoxyaluminum hydride reduction of **11** to a mixture of hydroxy esters, nmr 1.05 (d, J = 7, CH_3CHOH), which spontaneously lactonized in deuteriochloroform to give **13**: bp bath 98–100° (20 mm); ir (CCl$_4$) 1740 cm^{-1}; nmr 1.23 (s, angular CH_3), 1.33 (d, J = 7, CH_3CH), and 4.40 (octet, $J_{\text{H-CH}_3}$ = 7, $J_{\text{H-H}}$ = 8, CHCH$_3$), mass spectrum[13a] (70 eV) m/e 154 (M$^+$).



9

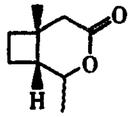


10, R = H
11, R = CH$_3$



12

Direct formation of the acid **10** in preference to the expected aldehyde is attributed[14] to the intervention of a labile ketol **14** since the neutral fraction from periodate oxidation of **9** contained predominantly the lactone acetal **15**: bp bath 45° (2 mm); ir (CH$_2$Cl$_2$) 1793 (lactone C=O), 1145, 1133, and 953 cm^{-1} (acetal); nmr 1.18 (s, angular CH_3), 1.28 (s, CH_3CCO), and 5.95 (m, half-width 4 Hz, acetal H); mass spectrum[13a] (70 eV) m/e 182 (M$^+$), which would result from direct cleavage of the tautomer of ketol **14**.



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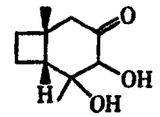

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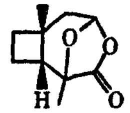

15

Alkylation of the keto acid **10** by inverse addition to a tetrahydrofuran–dimethyl sulfoxide (4:1) solution of methylenetriphenylphosphorane (2.5 equiv, 10 min) gave in 80% yield[15,16] the *cis*-olefinic acid **16**: nmr (CCl$_4$) 1.33 (s, 1-CH_3), 1.67 (broad s, vinylic CH_3), 4.66

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(6) (a) Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Commun.*, 423 (1966). The yield is improved to 55% by irradiating a 1% solution in benzene with a 450-W Hanovia high-pressure mercury-vapor lamp using a Pyrex filter (10 g requires 20 hr); (b) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, pp 855–856.

(7) Nmr spectra were measured (in deuteriochloroform at 60 MHz unless otherwise indicated) for each intermediate and were in agreement with the assigned structures. Chemical shifts are quoted in parts per million downfield from internal tetramethylsilane standard and coupling constants in hertz to the nearest 0.5 Hz.

(8) Gas chromatography was carried out with an F&M Model 402 using helium carrier gas with the following silanized diatomaceous earth (100–120 mesh) supported columns: (a) 2 m × 3 mm polyester (3% PDEAS); (b) 4 m × 3 mm polypropylene glycol (20% Ucon 90M); (c) preparative 3 m × 9 mm polypropylene glycol (10% Ucon 90M).

(9) Isolated by preparative gc using an all-glass modified Pye Model 105 instrument with a 10% nitrile silicone (XE-60) column supported on 5 m × 9 mm of silanized diatomaceous earth.

(10) This compound gave satisfactory elemental analytical data.

(11) R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, 21, 478 (1956).

(12) Rohm & Haas Co., Philadelphia, Pa.

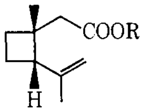
(13) We are grateful for these mass spectra measured by (a) Mr. J. Smith and Dr. L. Tökes, Syntex Research; (b) Mr. R. Ross and Dr. A. Duffield, Stanford University.

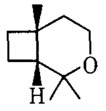
(14) *Cf.* P. Cohen and P. Mamont, *Bull. Soc. Chim. Fr.*, 1164 (1967).

(15) *Cf.* D. Taub, N. N. Girotra, R. D. Hoffsommer, C. H. Kuo, H. L. Slates, S. Weber, and N. L. Wendler, *Tetrahedron*, 24, 2443 (1968).

(16) Methylenation of the keto ester 11 in tetrahydrofuran to the corresponding isopropenyl ester also led to a 9:1 isomer mixture but in only 15% yield.

and 4.84 (broad s, two vinylic *H*), and 10.72 (COO*H*) contaminated by 3% of the undesired *trans* isomer as shown by gc analysis[8a] of the derived methyl esters **17**. Completion of the synthesis by reduction of **16** or **17** with sodium dihydridobis(2-methoxyethoxy)aluminate[17] in benzene–ether gave, after purification by preparative gc,[8a] the racemic pheromone **1**: bp bath 50° (12 mm); ir (CCl_4) 3610 (OH), 3075, 1645, and 892 cm^{-1} ($C{=}CH_2$); molecular ion found[13b] at *m/e* 154.13568 (calcd 154.13576). The nmr spectrum (CCl_4) of **1** showed resonances at 1.18 (s, 1-CH_3), 1.67 (broad s, vinylic CH_3), 1.88 (s, O*H*), 2.53 (t, J = 8.5, allylic *H*), 3.56 (t, J = 7, CH_2OH), 4.60 and 4.80 (broad s, two vinylic *H*) and established identity[18] with the natural product. Proof of the *cis* relationship (by reconnection) of side chains in **1** was obtained by treating[19] a 9:1 *cis–trans* isomer mixture of **1** with mercuric acetate (1 equiv) in dry tetrahydrofuran followed by aqueous alkaline sodium borohydride. The product was predominantly the cyclic ether[8c] **18** [nmr 1.02, 1.15, and 1.17 (three s, quaternary methyls) and 3.60 (m, CH_2O); molecular ion found[13b] at *m/e* 154.13581 (calcd 154.13576)], together with unchanged alcohol *trans* **1**, whose gc retention time[8b] (55.2 min) at 135° differed from that (54 min) of the pheromone **1**.


16, R = H
17, R = CH_3


18

When combined by Drs. D. D. Hardee and R. C. Gueldner (U. S. D. A., Boll Weevil Research Laboratory) with compounds **2**, **3**, and **4** for bioassay, the synthetic pheromone **1** showed activity in laboratory tests essentially identical with that of the natural product. We are most grateful for this determination.

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(17) J. Vit, B. Čásenský, J. Macháček, French Patent 1,515,582 (1967)

(18) Nmr spectra (CCl_4) of the natural product **1**, presented[6] by Dr. J. H. Tumlinson, show resonances at 1.22 (s), 1.72 (s), 2.59 (s, O*H*), 2.60 (broad t), 3.63 (t), 4.71, and 4.88 ppm. In contrast the *trans* isomer shows the quaternary methyl at 0.95 ppm.

(19) *Cf.* H. C. Brown and M. Rei, *J. Amer. Chem. Soc.*, **91**, 5646 (1969).

(20) Zoëcon Postdoctoral Fellow, 1968–1969.

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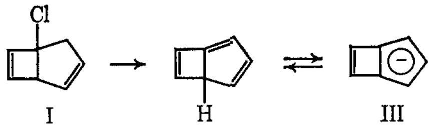
Antiaromatic Destabilization of Cyclobutadienocyclopentadienyl Anion

Sir:

We have reported[1] the observation that dehydrochlorination of I with KO-*t*-Bu produces a reactive triene II which dimerizes rapidly. We were also able to detect the equilibration of II with its anion III by observing deuterium exchange into II, producing dimers of II-d_1. It was originally suggested that a single Diels–Alder dimer was formed, but quickly discovered and reported[2] that a mixture of two dimers was actually formed by 2 + 2 addition of the strained double bond. Bauld has also shown[3] that this mixture of dimers is produced on generation of triene II, although curiously he did not observe deuterium exchange in II under our conditions. Cava has reported the preparation of a benzo derivative of III in solution.[4]


I
II
III

The pK_a of II is of interest since, of the five normal resonance structures for cyclopentadienyl anion, two of them in III would also have a cyclobutadiene ring structure. Thus if cyclobutadiene is "antiaromatic," *i.e.*, conjugatively destabilized,[5] this should lead to a high pK_a for II by comparison with cyclopentadiene. We wish to report that we have succeeded in preparing a solution of III, and have also determined an approximate pK_a for II which reveals strong destabilization in III by the cyclobutadiene ring fusion.

A solution of anion III was obtained by adding 200 mg (1.6 mmol) of I dropwise to 4 mmol of lithium dicyclohexylamide and 17 mmol of tetramethylethylenediamine in 25 ml of tetrahydrofuran at −75°. After brief warming to −20° the solution was cooled again to −75° and quenched[6] with D_2O, then acetic acid. A mixture of 40 mg of undeuterated I and 40 mg of the dimers derived from II was obtained. By nmr integration of the signal[1,3] at δ 6.4, the dimers are derived from II-d_1 (the illustrated H replaced by D) with less than 10% from II-d_0. Thus in this strongly basic medium II exists as the anion III.

An approximate pK_a of II was determined by attempted equilibration with hydrocarbons of known acidity. Thus, to the solution of III prepared as above was added 1 equiv of triphenylmethane (pK_a = 33).[7] After 5 min at −75°, the red color of triphenylmethyl anion did not appear and quenching with D_2O, as above, afforded the dimers of II-d_1 and undeuterated triphenylmethane. By contrast, equilibration of the solution of III with fluorene (pK_a = 25)[7] afforded fluorene-d_1 (by nmr integration) and undeuterated dimers of II. With xanthene (pK_a = 29)[7] the high reactivity of II caused major difficulties. Thus 250 mg of I was converted to the solution of anion III as described above and 354 mg (1 equiv) of xanthene was added. After equilibration for 10 min at −75°, quenching afforded only 7 mg of the dimers of II, and only 40 mg of recovered xanthene. With 5-min equilibration, 15 mg of the II dimers was obtained. However, in both experiments

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(1) R. Breslow, W. Washburn, and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 196 (1969).

(2) *Cf.* footnote 6 of M. P. Cava, K. Narasimhan, W. Zieger, L. J. Radonovich, and M. D. Glich, *ibid.*, **91**, 2378 (1969).

(3) N. L. Bauld, C. E. Dahl, and Y. S. Rim, *ibid.*, **91**, 2787 (1969).

(4) (a) See Cava, *et al.*, ref 2; (b) in unpublished work, we have detected the other possible benzo derivative of III, 1,2-cyclobutadienoindenyl anion, by a procedure similar to that in ref 1.

(5) *Cf.* R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967).

(6) Although carbanion equilibria may be disturbed during quenching in kinetically active solvents such as dimethyl sulfoxide, control studies such as those reported by R. Breslow and E. Mohacsi (*ibid.*, **85**, 431 (1963)) show that quenching with D_2O in solvents such as those used in the present study is a reliable assay for carbanion equilibria.

(7) These values are based on McEwen's acidity scale. *Cf.* D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 4.