

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

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

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: $a_i a_j + b_i b_j \cos \theta_{ij} = \delta_{ij}$, 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 Clementi¹⁸ 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 fol-

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

lowing linear relationship between C-C bond lengths and bond overlap is found.

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

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.

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

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 as-

(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).

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 ^{2.60}	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

suming 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 spⁿ-sp^m ($n, m = 1, 2, 3$) types.

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

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Synthetic Studies on Insect Hormones. IX.^{1,2} Stereoselective Total Synthesis of a Racemic Boll Weevil Pheromone

Sir:

Recent isolation³ of the sex attractant of the male boll weevil (*Anthonomus grandis* Boheman) followed a most difficult phase of insect pheromone research⁴ and allowed structure elucidation⁴ 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-

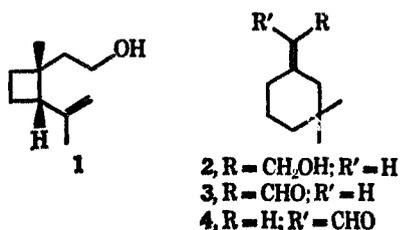
(1) Part VIII: see J. B. Siddall, M. Biskup, and J. H. Fried, *J. Amer. Chem. Soc.*, **91**, 1853 (1969).

(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).

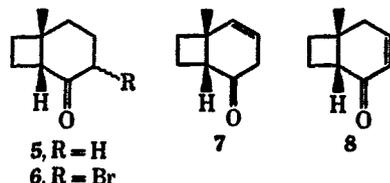
(5) Completion of a nonselective synthesis of **1** and its *trans* isomer was announced on Sept 10, 1969 at the 158th National Meeting of the American Chemical Society, New York, N. Y., by J. H. Tumlinson, D. D. Hardee, R. C. Gueldner, A. C. Thompson, P. A. Hedin, and J. P. Minyard, *Science*, **166**,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



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 spectrum⁷ 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% of the β,γ -unsaturated ketone⁹ 7: bp bath 45° (12 mm); ir (CCl₄) 1710 cm⁻¹; nmr 1.23 (s, CH₃) and 5.66 (broad s, 4 and 5-H) together with 73% of the required conjugated ketone¹⁰ 8: bp 45–47° (0.45 mm); uv max (cyclohexane) 223 (ϵ 7950) and 280 nm (ϵ 74); ir (CCl₄) 1670 cm⁻¹; nmr 1.33 (s, 6-CH₃), 6.12 (two t, $J_{3,4} = 10.5$, $J_{2,3} = 2$, 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.

The methyl of the envisioned acetyl group was introduced by ethereal methylolithium alkylation of 8 to give in quantitative yield a single isomer of a crystalline al-

(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.

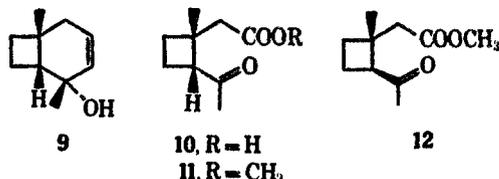
(8) Gas chromatography was carried out with an F&M Model 402 using helium carrier gas with the following silanized diatomaceous earth (100–120 mesh) supported columns: (a) 2 m \times 3 mm polyester (3% PDEAS); (b) 4 m \times 3 mm polypropylene glycol (20% Ucon 90M); (c) preparative 3 m \times 9 mm polypropylene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

(10) This compound gave satisfactory elemental analytical data.

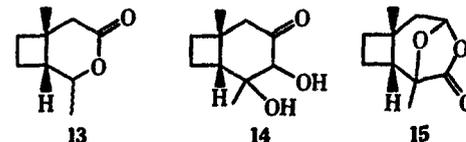
cohol¹⁰ 9: mp 60–61°; ir (CCl₄) 3600 cm⁻¹; nmr 1.1^c, 1.19 (two s, 2-CH₃ and 6-CH₃), and 5.84 (m, half-width 4 Hz, 3-H and 4-H).

Ring opening of the *cis*-olefinic alcohol 9, carried out by osmium tetroxide catalyzed sodium periodate oxidation¹¹ at 20° for 15 hr in ether–water (1:1), was suffi-



ciently mild to afford a single *cis*-keto acid 10:¹⁰ bp 58–60° bath (0.05 mm); ir (CCl₄) 3515 (free OH), 3400–2500, and 1708 cm⁻¹; nmr 1.41 (s, 1-CH₃), 2.11 (s, COCH₃), 2.51 (s, CH₂COOH), 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-400¹² 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, CH₃) and 2.57 (s, CH₂) for the *trans*-isomer^{8c} 12, but proof of *cis* stereochemistry of 11 came from rapid lithium *t*-butoxyaluminum hydride reduction of 11 to a mixture of hydroxy esters, nmr 1.05 (d, $J = 7$, CH₂CHOH), which spontaneously lactonized in deuteriochloroform to give 13: bp bath 98–100° (20 mm); ir (CCl₄) 1740 cm⁻¹; nmr 1.23 (s, angular CH₃), 1.33 (d, $J = 7$, CH₂CH), and 4.40 (octet, $J_{H-CH_2} = 7$, $J_{H-H} = 8$, CHCH₃), mass spectrum^{13a} (70 eV) m/e 154 (M⁺).

Direct formation of the acid 10 in preference to the expected aldehyde is attributed¹⁴ to the interven-



tion 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 (CH₂Cl₂) 1793 (lactone C=O), 1145, 1133, and 953 cm⁻¹ (acetal); nmr 1.18 (s, angular CH₃), 1.28 (s, CH₂CCO), 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.

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 (CCl₄) 1.33 (s, 1-CH₃), 1.67 (broad s, vinylic CH₃), 4.66

(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.

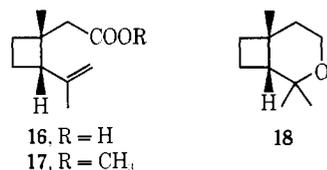
(13) We are grateful for these mass spectra measured by (a) Mr. J. Smith and Dr. L. Tökes, Syntex Research; (b) Mr. R. Ross and Dr. A. Duffield, Stanford University.

(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. Slaters, 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 (COOH) contaminated by 3% of the undesired *trans* isomer as shown by gc analysis^{3a} of the derived methyl esters **17**. Completion of the synthesis by reduction of **16** or **17** with sodium dihydridobis(2-methoxyethoxy)aluminate¹⁷ in benzene-ether gave, after purification by preparative gc,^{3a} the racemic pheromone **1**: bp bath 50° (12 mm); ir (CCl₄) 3610 (OH), 3075, 1645, and 892 cm⁻¹ (C=CH₂); molecular ion found^{18b} at *m/e* 154.13568 (calcd 154.13576). The nmr spectrum (CCl₄) of **1** showed resonances at 1.18 (s, 1-CH₃), 1.67 (broad s, vinylic CH₃), 1.88 (s, OH), 2.53 (t, *J* = 8.5, allylic *H*), 3.56 (t, *J* = 7, CH₂OH), 4.60 and 4.80 (broad s, two vinylic *H*) and established identity¹⁸ with the natural product. Proof of the *cis* relationship (by reconnection) of side chains in **1** was obtained by treating¹⁹ 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, CH₂O); molecular ion found^{18b} 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**.

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.

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

(18) Nmr spectra (CCl₄) of the natural product **1**, presented⁵ by Dr. J. H. Tumlinson, show resonances at 1.22 (s), 1.72 (s), 2.59 (s, OH), 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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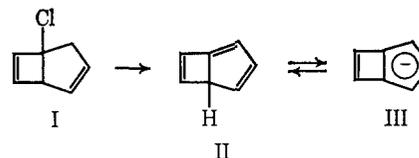
Antiaromatic Destabilization of Cyclobutadienocyclopentadienyl Anion

Sir:

We have reported¹ 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 reported² that a mixture of two dimers was actually

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

formed by 2 + 2 addition of the strained double bond. Bauld has also shown³ 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



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 quenched⁶ with D₂O, 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 D₂O, 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

(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-cyclobutadienocyclopentadienyl 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. Mohacsy (*ibid.*, **85**, 431 (1963)) show that quenching with D₂O 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.