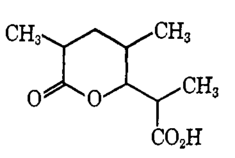
This interpretation is in agreement with the earlier finding that pikromycin when heated with 1 *N* barium hydroxide gives almost 1 equiv of barium carbonate and a "base-insoluble oil."[11]

The substitution pattern of pikromycin at C_3–C_9, as shown in **5**, and of kromycin, as shown in **6**, can be deduced from the following facts: Prelog, *et al.*, have shown that pikromycin as well as methymycin (**1**) and narbomycin (**7**) yield lactone **8** upon oxidation with potassium permanganate in acetone.[12] Furthermore, kromycin upon ozonolysis is degraded to pentane-2,3-dione,[4] and its high-resolution mass spectrum shows an intense peak at *m/e* 152 (152.0840; calcd for $C_9H_{12}O_2$: 152.0840), which is consistent with the ion **9**. Therefore kromycin must have a double bond between C_4 and C_5 and not alternatively between C_7 and C_8.[13] This double bond gives rise to a doublet (1 H, δ 6.30, d, J = 11 Hz) not found in the spectrum of pikromycin. In addition a methyl singlet (3 H, δ 1.90, s) has moved out of the multitude of signals between 0.88 and 1.51 in pikromycin.



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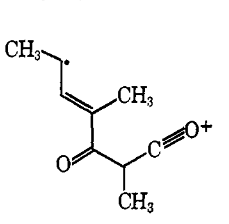

9

Pikromycin has a double bond conjugated to a carbonyl group, as indicated by its uv and ir spectra.[4,5] This double bond, bearing two hydrogen atoms, is *trans* as shown in the nmr spectrum (2 H, δ 6.26 and 6.70; dd; J = 16 Hz). Degradation of pikromycin to kromycin leaves this double bond unchanged (2 H, δ 6.05 and 6.72; dd; J = 16 Hz). This proves the substitution pattern at C_{10} and C_{11} in pikromycin and kromycin as is shown in structures **5** and **6**, respectively.

The tertiary hydroxy group of pikromycin and kromycin[4,5] must be placed at C_{12} on the basis of chemical[5] and nmr evidence,[14] because the nmr spectrum of kromycin shows only one proton in an area characteristic for a proton bonded to carbon that bears an oxygen function. This has to be the proton at C_{13}, since it appears as a pair of doublets in the nmr spectrum (1 H, δ 4.87 and 4.93; J = 3 Hz) which is typical for a proton coupled to two diastereotopic[15] protons. This further indicates that the ethyl group of pikromycin and kromycin has to be placed at C_{13}, as already shown by chemical evidence,[4,5] *i.e.*, formation of propionaldehyde upon treatment of kromycin with sodium hydroxide and also upon oxidation of the lithium aluminum hydride reduction product of kromycin with periodic acid.

Structure **5** for pikromycin explains why pikromycin can be degraded to its anhydro aglycone, kromycin (**6**), whereas under similar conditions no defined product could be obtained from narbomycin (**7**).[16] The lactone ring in narbomycin (**7**) can be opened up by β elimination. This reaction is not possible in pikromycin because of the hydroxy group at C_{12}.

Attempts to exchange the proton at C_2 in pikromycin (**5**) and kromycin (**6**) with D_2O in chloroform–pyridine at room temperature were unsuccessful even after several days. This indicates that the macrocyclic rings of **5** and **6** are extremely rigid due to nonbonded interactions and that C_2 behaves like a bridgehead carbon atom. The rigidity of the kromycin ring shows up also in the nmr spectrum, since there is no significant difference in the nmr spectra taken at room temperature and at 160°.[17]

Acknowledgments. We are grateful to the National Institutes of Health (Grant No. FR-00355) for providing a MS-9 mass spectrometer and the National Science Foundation (Grant No. GP 6626) for general financial support. We also wish to thank Professor V. Prelog for supplying us with samples of pikromycin and kromycin.

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[11] H. Brockmann and R. Strufe, *Chem. Ber.*, **86**, 876 (1953).

[12] R. Anliker, D. Dvornik, K. Gubler, H. Heusser, and V. Prelog, *Helv. Chim. Acta*, **39**, 1785 (1956).

[13] A homologous series of ions in the mass spectrum of kromycin at *m/e* 96, 109, 138, and 123 is in accord with this structural assignment.

[14] The proton of this hydroxy group appears as a broad singlet (δ 3.08) in the nmr spectrum and is easily exchanged with D_2O.

[15] K. Mislow, "Topics in Stereochemistry," Vol. I, Interscience Publishers, New York, N. Y., 1967.

[16] V. Prelog, A. M. Gold, G. Talbot, and A. Zamojski, *Helv. Chim. Acta*, **45**, 4 (1962).

[17] Nmr spectra taken in 1-chloronaphthalene.

[18] National Institutes of Health Predoctoral Fellow, 1967–present.

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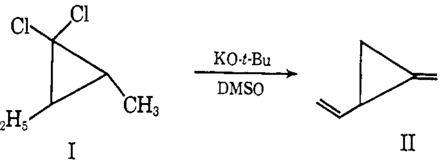
Vinylmethylenecyclopropane

Sir:

The syntheses of variously substituted methylenecyclopropanes have been reported in recent years. The thermal rearrangement of these compounds is of special interest due to the intermediacy of the trimethylenemethane system.[1] Vinylmethylenecyclopropane is of interest in this regard and, to our knowledge, has never been synthesized. We wish to report its properties and preparation *via* the useful technique of base-induced elimination–isomerization of readily obtainable *gem*-dichlorocyclopropanes.[2,3]

When 1,1-dichloro-2-ethyl-3-methylcyclopropane (I) was added slowly to a solution of potassium *t*-butoxide in dimethyl sulfoxide (1.7-hr reaction time), vinylmethylenecyclopropane (II) was obtained (62% yield)



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[1] W. Moffitt, *Trans. Faraday Soc.*, **45**, 373 (1949); J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Amer. Chem. Soc.*, **74**, 4579 (1952); H. H. Greenwood, *Trans. Faraday Soc.*, **48**, 677 (1952); P. Dowd, *J. Amer. Chem. Soc.*, **88**, 2587 (1966), and references cited therein.

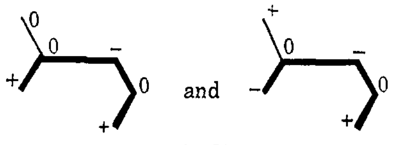
[2] Compounds I and IV[3] were prepared from 2-pentene and 2-methyl-2-hexene, respectively, by treatment with potassium *t*-butoxide and chloroform in *n*-pentane; *cf.* T. C. Shields and P. D. Gardner, *J. Amer. Chem. Soc.*, **89**, 5425 (1967).

[3] All compounds reported gave satisfactory elemental analyses.

after an aqueous quench, pentane extraction, and distillation. Final separation from the pentane was accomplished by glpc.[4]

The nmr spectrum of II shows multiplets at δ 1.0, 1.46, and 2.0 (1 H each) and a complex olefinic pattern from 4.7 to 5.8 (5 H). Its infrared spectrum displays characteristic olefinic bands at 6.12 and 11.2 μ (broad).

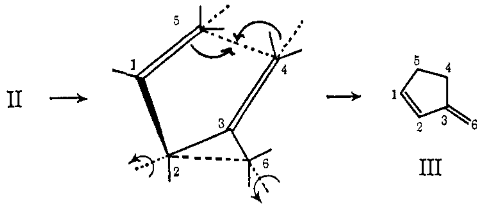
The possibilities for a thermal rearrangement are of interest since the intermediate 2-methylenepentadienyl diradical is orbitally degenerate.[5] The relative signs of the atomic orbital contributions to these degenerate states indicate that maintenance of orbital symmetry[6] would not lead to a preferred course for molecular rearrangement.



sign of AO's in
degenerate MO's

Such a thermal process, by analogy to the formation of trimethylenemethane-type intermediates from methylenecyclopropanes,[7] should occur at high temperatures. However, when II is heated as a dilute pentane solution ($\sim$15%) at 80° for 13 hr there is more than 90% thermal rearrangement. The rearranged product, bp 43° (217 mm), $\lambda_{\max}^{C_6H_{12}}$ 234 mμ (ϵ 17,900), displays nmr multiplets at δ 2.47 (4 H), 4.79 (2 H), and 6.12 (2 H). These data are only consistent with 3-methylenecyclopentene.

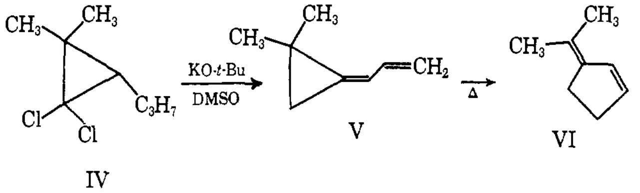
The moderate conditions for conversion suggest that a planar diradical is not an appropriate intermediate. The carbon skeleton of II is not planar but must undergo rotation about several bonds to reach the planar product III.



The structure which gives a maximum vinyl–cyclopropyl conjugation leaves the two double bond systems essentially orthogonal. Thus as ring opening occurs,[8] the terminal orbital of the vinyl group (5), with the correct sign for bonding to the *exo*-methylene location (4) and the AO of 4, rotate to form the final ring σ bond (4–5). The transition state for this process is quite analogous to the thermal Cope rearrangement of 1,5-hexadiene,[5b] *i.e.*, two allyl radicals. The two three-atom conjugated systems, formed by rotation about the bond 3–6, are mutually orthogonal and attached along bond 2–3. The signs of the highest occupied allyl orbitals allow construction of the path both in ring opening and ring closing. Since the final π system (1–2–3–6) is conjugated and comes from these allyl orbitals, π-orbital symmetry is maintained if the two ends of the different allylic systems, which end up in the π system and on the same face of the product, are of opposite sign. Two operations are necessary to meet the requirements within the stereochemical framework (counterclockwise, ccw, direction refers to the enantiomer considered in the conversion II → III): (*i*) *conrotatory cyclopentene ring closure* (*ccw at both 4 and 5*) *and* (*ii*) *conrotatory cyclopropane ring opening* (*ccw about both 2–3 and 3–6 bonds*).[9] The stereochemistry of II gives a favorable orientation so that both processes can occur in a concerted fashion; thus, considerable stabilization of the transition state allows a low temperature but stereospecific conversion.

In order to obtain further chemical evidence for this process, the properties of II were compared with a methylenecyclopropane in which the vinyl group was attached to the methylene carbon, *i.e.*, an allylidenecyclopropane.

1,1-Dichloro-2,2-dimethyl-3-propylcyclopropane (IV)[2] was introduced dropwise at 30° into a solution containing potassium *t*-butoxide in dimethyl sulfoxide. After 2 hr the mixture was quenched with ice water and extracted with pentane. Fractional distillation afforded a 60% yield of 2,2-dimethylallylidenecyclopropane (V), $\lambda_{\max}^{C_6H_{12}}$ 230 mμ (ϵ 21,875), whose molecular weight was determined as 108 mass spectrally. The nmr spectrum of V consists of multiplets centered at δ 6.30 (2 H) and 5.10 (2 H), sharp singlets at 1.23 and 1.19 (6 H total), and a multiplet at 0.98 (2 H).



Compound V undergoes isomerization at 190°[10] to 3-isopropylidenecyclopentene (VI), $\lambda_{\max}^{C_6H_{12}}$ 246 mμ (ϵ 13,060). The nmr spectrum displays multiplets centered at δ 6.32 and 5.90 (1 H each), 2.43 (4 H), and 1.70 (6 H). The ir spectrum of VI is superimposable with that of 3-isopropylidenecyclopentene prepared by another method.[11]

The rearrangement process of V differs significantly from that of II since the former planar system may rearrange *via* the nonstereospecific diradical originally discussed.[12] Calculations are in progress to confirm the basic rearrangement routes predicted by orbital symmetry.

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(4) Isolation was performed using a 0.5 in. × 10 ft column filled with Varian FFAP packing (15%) operated at 45°.

(5) (a) J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **89**, 4532 (1967). W. von E. Doering and W. R. Doblier, Jr., *ibid.*, **89**, 4534 (1967), have observed another orbitally degenerate diradical system. (b) W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, 2, 115 (1963).

(6) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(7) J. P. Chesick, *J. Amer. Chem. Soc.*, **85**, 2720 (1963).

(8) An alternative process which forms the same product, a 1,3-sigmatropic shift of the ring-bonded atom (6 in the conversion II → III) to the terminal vinyl position 5, is not allowed.[6]

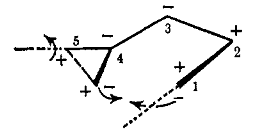
(9) Consecutive or concerted disrotatory processes (other, conrotatory–disrotatory or disrotatory–conrotatory, rotational combination alternatives are forbidden) do not give the intermediate orbital which converts to the highest filled π orbital of the product.

(10) Isomerization occurs on a 0.5 in. × 6 ft 30% SE-30 silicone gum rubber column above 160°.

(11) D. W. Peck, *et al.*, Abstracts, 19th Annual Southeastern Regional Meeting of the American Chemical Society, Nov 1–3, 1967, No. 245.

Acknowledgments. The authors thank Dr. W. T. Pace for nmr results and Mr. C. O. Allen for ultraviolet spectra.

(12) It is possible, using inversion[6] at the atom which breaks and makes a ring σ bond, to formulate a concerted reaction involving disrotation at the *exo* position in the initial and final states.



π AO sign					
5	4	3	2	1	atom
	−	−	+	+	reactant
+	0	−	0	+	intermediate
+	+	−	−		product

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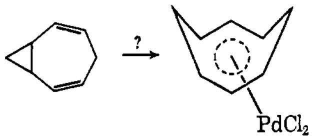
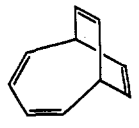
The Rearrangement of Bullvalene–Palladium Chloride Complex

Sir:

Numerous 1,4- and 1,5-dienes form palladium chloride π complexes in which the chlorine ligands remain attached to palladium.[1] On the other hand, conjugated acyclic dienes[2a,b] and vinylcyclopropanes[2c] react with palladium chloride to form π-allyl complexes in which a chlorine atom is transferred to carbon. In the case of homotropilidenes, both types of behavior are conceivable, but in addition there exists the intriguing possibility that all six homotropilidene π electrons can interact with palladium to yield a pseudoarene complex such as **1**. During our efforts to determine the structure of homotropilidene–palladium chloride complexes we have encountered a facile rearrangement of bullvalene to bicyclo[4.2.2]deca-2,4,7,9-tetraene (**2**), which is the subject of this communication.[3]



1

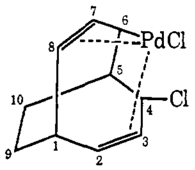


2

Treatment of bullvalene[4] with 1 equiv of bis(benzonitrile)palladium dichloride[5] at room temperature results in rapid precipitation of a dark, amorphous solid with the expected displacement of benzonitrile. After filtration, the solid is treated with aqueous pyridine or dimethyl sulfoxide to liberate the complexed hydrocarbons. Analysis of the products by glpc shows a single major component, isolated in 60% yield, which is identical with bicyclo[4.2.2]deca-2,4,7,9-tetraene (**2**).[6] Small amounts of naphthalene and *cis*-9,10-dihydronaphthalene[7] are also present, as shown by spectral and glpc comparison with authentic samples, but no trace of bullvalene can be detected. However, the rearrangement can be suppressed completely by repeating the experiment at −40°. Under these conditions, an orange complex (**3**) is formed in quantitative yield, and treatment of **3** with dimethyl sulfoxide results in recovery of 95% of the starting bullvalene. The crystalline bullvalene–palladium chloride complex **3** is stable for short periods at 0°, but all efforts to prepare solutions of **3** resulted in rearrangement.

The conversion of bullvalene to bicyclo[4.2.2]deca-2,4,7,9-tetraene also takes place catalytically. This variation constitutes a practical synthesis of **2**, since at low conversion **2** is the sole product. With longer reaction times and more catalyst, naphthalene and 9,10-dihydronaphthalene can be detected.[8] Control experiments show that these side products are also formed from purified **2**, thereby substantiating the view that **2** is the *sole initial* rearrangement product of bullvalene–palladium chloride complex **3**.

Since the complex **3** is too unstable for spectral studies, the palladium chloride complex **4**[9] of dihydrobullvalene[4] was prepared as a model for **3**. The nmr spectrum of **4** (Table I) is in accord with an unsymmetrical structure in which the cyclopropane ring is no longer intact,[2c] as shown by the number of low-field hydrogens. Of several isomeric structures which are possible, only **4** is consistent with chemical shift[10,11] and



4

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(1) M. Dub, "Organometallic Compounds," Vol. 1, 2nd ed, Springer-Verlag Inc., New York, N. Y., 1966, pp 865–866; H. Dietl and P. M. Maitlis, *Chem. Commun.*, 759 (1967); E. E. van Tamelen and D. Carty, *J. Am. Chem. Soc.*, **89**, 3922 (1967); H. Frye, E. Kuljian, and J. Viebrock, *Inorg. Nucl. Chem. Letters*, **2**, 119 (1966); J. C. Trebellas, J. R. Olechowski, and H. B. Jonassen, *J. Organometal. Chem.* (Amsterdam), **6**, 412 (1966).

(2) (a) B. L. Shaw, *Chem. Ind.* (London), 1190 (1962); (b) M. Donati and F. Conti, *Tetrahedron Letters*, 1219 (1966); (c) J. A. Braatz and A. D. Ketley, *J. Organometal. Chem.* (Amsterdam), **9**, P5 (1967); T. Shono, T. Yoshimura, Y. Matsumura, and R. Oda, *J. Org. Chem.*, **33**, 876 (1968).

(3) A similar rearrangement appears to occur upon treatment of bullvalene with iron carbonyl: G. N. Schrauzer, P. Glockner, and R. Merenyi, *Angew. Chem. Intern. Ed. Engl.*, **3**, 509 (1964). Related findings are described by U. Kruerke, *ibid.*, **6**, 79 (1967), and by G. N. Schrauzer and P. Glockner, *J. Am. Chem. Soc.*, **90**, 2800 (1968). Stable silver complexes of bullvalene have been prepared: A. Allerhand and H. S. Gutowski, *ibid.*, **87**, 4092 (1965); J. S. McKechnie, M. G. Newton, and I. C. Paul, *ibid.*, **89**, 4819 (1967).

(4) G. Schröder, *Ber.*, **97**, 3140 (1964).

(5) M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938).

(6) M. Jones, Jr., and L. T. Scott, *ibid.*, **89**, 150 (1967). We are grateful to Professor Jones for providing spectra of **2**.

(7) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

(8) The following procedure is useful for the preparation of bicyclo[4.2.2]decatetraene: Bullvalene (2.26 g) in dry chloroform (30 ml) is refluxed for 3 hr with bis(benzonitrile)palladium dichloride (0.07 g, 0.02 equiv). Most of the chloroform is then distilled off using a Vigreux column, and the residue is separated by preparative tlc on silica gel (100 cm × 20 cm, 1.5 mm layer) with hexane to afford starting bullvalene (0.36 g, R_f 0.3), **2** (1.5 g, R_f 0.45), and a zone containing naphthalene and 9,10-dihydronaphthalene in a 4:1 ratio (0.3 g, R_f 0.55).

(9) Dihydrobullvalene can be recovered from **4** upon treatment with cold pyridine, but solutions of the complex decompose gradually at room temperature.

(10) The chemical shift (τ 4.2) of H_8 is at least 1 ppm too low for consideration of a π-allyl structure for **4**: K. C. Ramey and G. L. Statton, *J. Am. Chem. Soc.*, **88**, 4387 (1966); R. Hüttel, H. Christ, and K. Herzog, *Ber.*, **97**, 2710 (1964).

(11) The nmr spectrum of **4** is reversibly temperature dependent below the decomposition point of 60°. The chemical shifts of H_6 and H_8 gradually converge (H_6, τ 7.0 and H_8, τ 3.9 at −50°; H_6, τ 5.5 and H_8, τ 4.3 at 60°), indicating increased bonding between C_8 and palladium at higher temperatures.