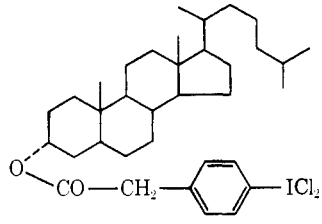
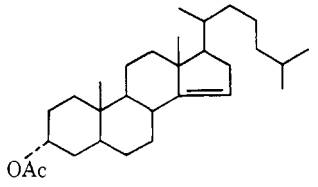
predominantly intramolecular remote functionalization. The *p*-iodophenylacetic ester,[8] mp 95–97°, of 3α-cholestanol was converted with Cl_2 to the corresponding dichloride III. Irradiation of a 0.33×10^{-3} *M* solution



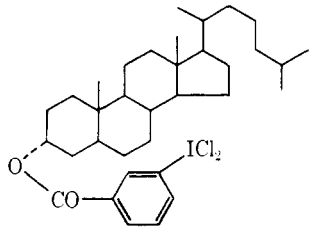
III



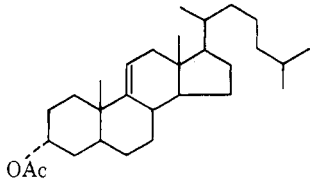
IV

of ester III in chlorobenzene at −25° with a sun lamp, followed by hydrolysis and work-up as above, yielded 20% of recovered cholestanol (acetate) and 53% of Δ14-cholestenyl 3α-acetate (IV) identical with authentic material.[6] In addition only 5% of the Δ9(11) isomer and 0.8% of the Δ5 isomer were detected, along with polar and unidentifiable material. These other isomers must have been formed in a competing *inter*molecular process, since 0.33×10^{-3} *M* androstane included in the reaction mixture as a control was converted to 9% of the expected mixture of androstenes. The *intra*molecular process is apparently completely selective for C-14; more intermolecular, randomized, halogenation is seen at room temperature or with higher concentrations.

Remote oxidation by benzophenone esters attached to 3α occurs at C-14 with some para derivatives but in ring B with the corresponding meta esters.[7] This proves to be true for attached $PhICl_2$ as well. Thus 3α-cholestanyl *m*-iodobenzoate,[8] mp 89.5–90.5°, was converted to the dichloride V and irradiated in benzene at



V



VI

1.0×10^{-3} *M* and room temperature. After hydrolysis, etc., 35% of 3α-cholestanol (acetate) was recovered, and 43% of Δ9(11)-cholestenyl 3α-acetate (VI) was isolated, mp 80.5–82°, which was hydrolyzed to the known[6] Δ9(11)-3α-cholestenol. Only 9% of the Δ14 isomer was formed and 2% of the Δ5 olefin. In a control reaction, androstane at 1.0×10^{-3} *M* was 20% functionalized, so the *inter*molecular process has not been completely suppressed. The yield of VI and conversion of V are even higher for reaction in CH_2Cl_2.

The selective attack at C-14 in III, and C-9 in V, is consistent with predictions from molecular models assuming that hydrogen abstraction is done by the chlorine atom in the [Ar–I–Cl]· intermediate.[9] The chlorine atom in the intermediate derived from III is in fact in essentially the same place as is the abstracting oxygen in the *p*-benzophenoneacetic ester of 3α-cholestanol, whose photolysis also produced a Δ14-3α-cholestanol derivative.[6] The present work not only furnishes alternative and convenient approaches to this olefin and to the important Δ9(11) unsaturation but it also demonstrates that the principles we have developed in connection with intramolecular benzophenone photochemistry can be extended to impose orientation factors on radical chain processes.[10]

(8) Characterized by analysis and pmr spectrum.

(9) D. D. Tanner and P. B. van Bostelen, *J. Org. Chem.*, **32**, 1517 (1967), suggest abstraction by iodine to form an unstable tricovalent iodine derivative which then loses HCl. Such a mechanism looks energetically unfavorable and is not geometrically possible for III.

(10) Financial support of this work by the National Institutes of Health and an NSF predoctoral fellowship to R. C. are gratefully acknowledged.

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Stereochemistry of the Di-π-methane Rearrangement at the Methane Carbon. Mechanistic and Exploratory Organic Photochemistry[1]

Sir:

In our earlier studies on the di-π-methane rearrangement,[1-4] we found that retention of configuration is the preferred stereochemistry at carbons 1 and 5 of the 1,4-pentadiene system. We did encounter some evidence in constrained systems[5] pointing toward a preference for inversion of configuration at the one other stereochemical center, namely the methane carbon (*i.e.*, C-3). Mariano in his elegant studies has attacked the problem from another perspective and demonstrated that in constrained di-π-methane systems it is possible to enforce either retention or inversion of configuration.[6]

The present research aimed at determination of the preferred C-3 stereochemistry in an unconstrained, acyclic system. For this we selected 3-ethyl-3,5-dimethyl-1,1-diphenyl-1,4-hexadiene (**1**). It was found that the di-π-methane rearrangement of ethylmethyldiene **1** led to *cis*- and *trans*-3-ethyl-3-methyl-2-(2′-methylpropenyl)-1,1-diphenylcyclopropane (**2a** and **b**) with a quantum yield of 0.11. Optically active ethylmethyldiene **1** was prepared as were optically active *cis*- and *trans*-vinylcyclopropanes **2a** and **2b**.[7] The con-

(1) Paper LXXXV of the series. For the previous paper note H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *J. Amer. Chem. Soc.*, **96**, 1459 (1974).

(2) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.* **73**, 531 (1973).

(3) H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 6267 (1970).

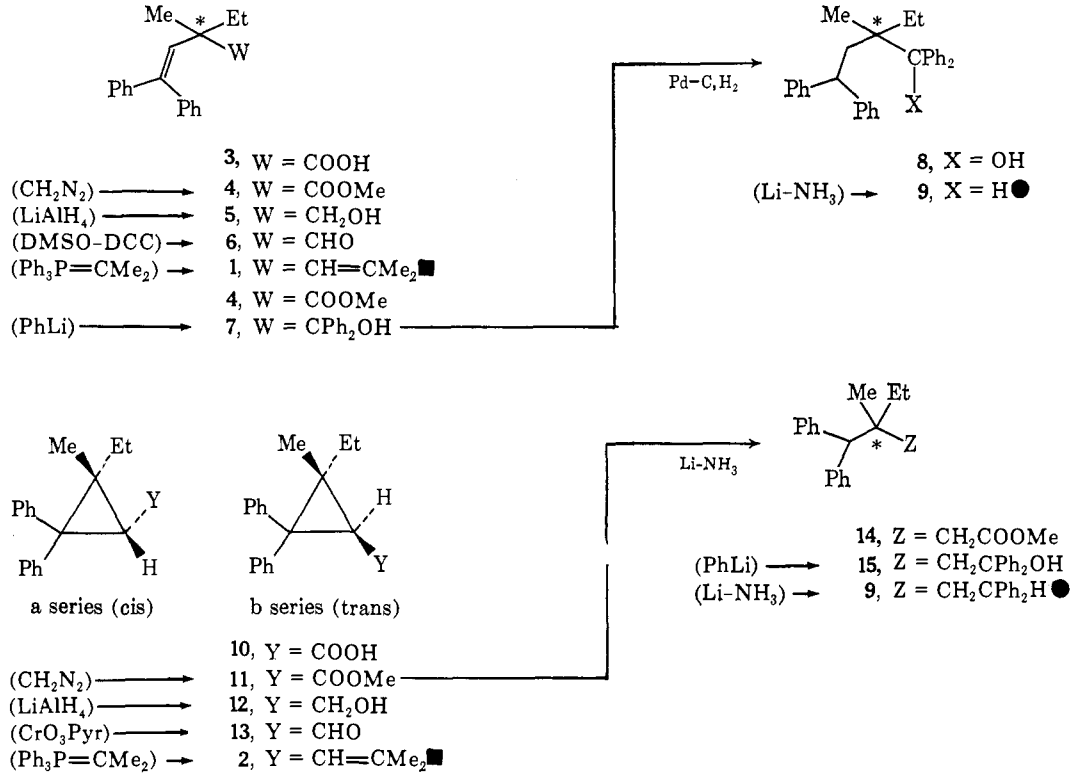
(4) H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *J. Amer. Chem. Soc.*, **94**, 5504 (1972).

(5) (a) H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **92**, 1411 (1970); (b) *ibid.*, **94**, 8749 (1972); (c) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **89**, 5971 (1967); (d) *ibid.*, **91**, 5307 (1969); (e) H. E. Zimmerman, P. Hackett, D. F. Juers, J. M. McCall, and B. Schröder, *ibid.*, **93**, 3653 (1971).

(6) (a) P. S. Mariano and J. Ko, *J. Amer. Chem. Soc.*, **94**, 1766 (1972); (b) P. S. Mariano and R. B. Steitle, *ibid.*, **95**, 6114 (1973).

(7) All compounds gave satisfactory elemental analyses. Complete synthetic and experimental details will be given in our full paper.

Chart I. Scheme Used for Interrelating Configurations



■Compounds being configurationally related
●Compound common to both series.

figurations were related using the sequences depicted in Chart I (for brevity where reactions involve no skeletal change but only interchange of functional groups the transformations and reagents are shown beneath each structure).

The relating scheme relies upon interconversion of ethylmethyldiene **1** and the *cis*- and *trans*-vinylcyclopropanes **2a** and **2b** with the same compound, 3-diphenylmethyl-3-methyl-1,1-diphenylpentane (**9**). The transformations were selected to avoid disturbing the ethylmethyl center. When carried out with optically active compounds, it was found that (−67.5°) ethylmethyldiene **1**, (−286°) *cis*-vinylcyclopropane **2a**, and (+490°) *trans*-vinylcyclopropane **2b** all had the same ethylmethyl configuration. The given rotations are at 365 nm but specific rotations at four other wavelengths and also ORD curves were used to confirm the relationship and to demonstrate the absence of optically active impurities.

After photolysis of optically active (−)-ethylmethyldiene **1**, the *cis*- and *trans*-vinylcyclopropane products (**2a** and **b**) were separated by recycling high-pressure liquid chromatography. The rotations obtained for cis and for trans isomers corresponded to 97.5 and 98.0% inversion of configuration. The 2.5 and 2.0% differences from total inversion were on the borderline of experimental error but were found to arise from loss of activity during the recycling process.

Thus, in the di-π-methane rearrangement of ethylmethyldiene **1**, the ethylmethyl center is inverted. We can picture the rearrangement as shown in eq 1.

This provides knowledge of the stereochemistry at the last unknown center in the di-π-methane rearrangement.

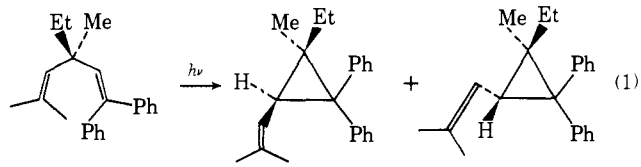
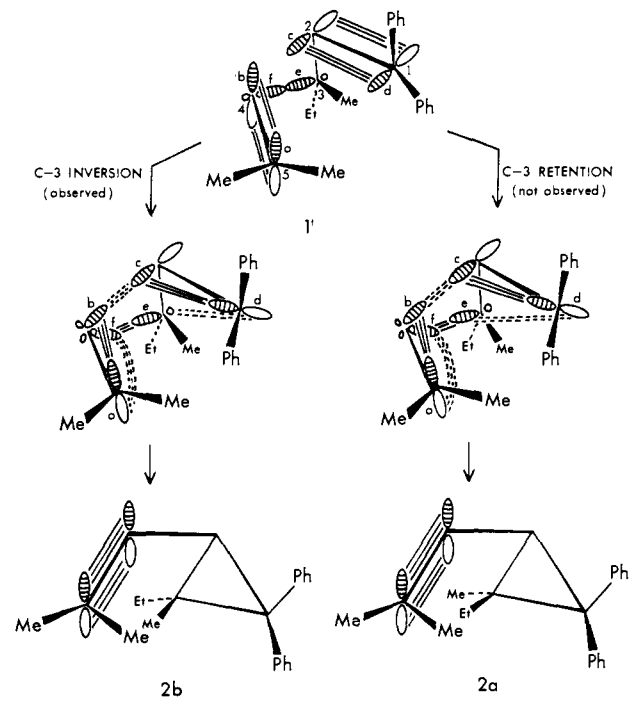
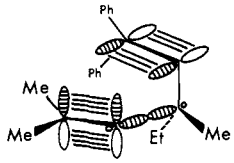


Chart II. Basis Orbital Array and Alternative Reaction Mechanisms[a]



[a] Original bonds breaking (≡) and new bonds forming (⋮⋮⋮).

We are now able to decide which of two alternative cyclic arrays is actually preferred. The mechanisms in terms of the six orbital array are given in Chart II. For simplicity only one reactant conformation is followed through the reaction (*i.e.*, **1′**); this is one leading to the trans product *via* the C-3 inversion route but to the cis product *via* the C-3 retention mechanism. Conformer **1″** can be seen to lead to the cis product *via*



1″

alternative conformer of ethylmethyldiene **1**

the inversion route and trans product *via* the retention pathway. Further conformers are also possible. However, the C-3 inversion *vs.* retention question is independent of reactant conformation.

It is seen that the observed C-3 inversion mechanism has a six-electron Möbius array while the C-3 retention process has a six-electron Hückel cycle of basis orbitals. Only the Möbius array provides an allowed photochemical pathway.[8,9] The reaction can be alternatively analyzed as ${}_{\sigma}2_{a} + {}_{\pi}2_{a} + {}_{\pi}2_{a}$ which is more favorable than the ${}_{\sigma}2_{s} + {}_{\pi}2_{a} + {}_{\pi}2_{a}$ (*i.e.*, the retention mechanism). However, the two analyses really are identical, since a process with an odd number of a's in the Woodward–Hoffmann approach[10] will necessarily be Möbius[8] and one with an even number of a's will be Hückel.[8] In any case, the allowed mechanism is the one followed.

Acknowledgment. Appreciation is expressed to the National Science Foundation, to the National Institutes of Health (Grant GM 07487), and the U. S. Army Research Office (Durham) for support of this research. National Institutes of Health Predoctoral Fellowships to J. D. R. and L. R. S. and a Science Research Council Postdoctoral Fellowship to C. J. S. are gratefully acknowledged.

(8) (a) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966); (b) H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971).

(9) The qualitative valence bond picture we have used previously[2-5] is in no way inconsistent with the cyclic orbital array. The former merely gives resonance contributors of varying importance along the reaction coordinate.

(10) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

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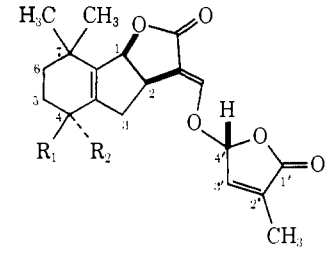
The Total Synthesis of *dl*-Strigol

Sir:

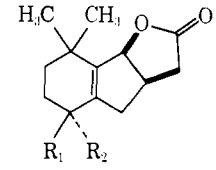
Strigol, a highly potent seed germination stimulant for the root parasite witchweed (*Striga lutea* Lour.), was isolated from the root exudates of cotton (*Gossypium hirsutum* L.) in 1966 by Cook, *et al.*[1] However, the structure and relative configuration of strigol, as depicted in **1**,[2] have only recently been derived on the basis of spectroscopic and X-ray crystallographic data.[3] The occurrence of similar stimulants in several plants suggests that strigol may be representative of a new class of plant hormones.[3] The unavailability of strigol from natural sources in quantities sufficient for biological studies aroused our interest in the chemical synthesis of this molecule. We now wish to report the first total synthesis of *dl*-strigol.

Conceptually, the most direct synthetic approach would lie in the preparation of hydroxylactone **3** followed by formylation and subsequent O-alkylation. As the stereochemistry of O-alkylation of β-dicarbonyl compounds can be profoundly influenced by solvent effects,[4] it seemed likely that the stereochemistry about the enol ether double bond would be subject to some control. To test this crucial final step in the synthetic sequence, we examined the alkylation of the model hydroxymethylene lactone **5**[5] with the bromobutenolide **9** which was prepared from 3-methyl-2-furoic acid (**6**)[6] in the following manner. Photochemical oxygenation of **6** in ethanol[7] gave (after $SnCl_2$ reduction of peroxides) the lactone acetal **7**[8] (80%). Hydrolysis to the lactol **8**[8] (H_2O, reflux, 0.5 hr, 90% yield) followed by treatment with triphenylphosphine and carbon tetrabromide in dichloromethane[9] (0°, 5 hr) afforded the required bromobutenolide **9**[10] (65–70%, bp 54° (0.4 mm)).

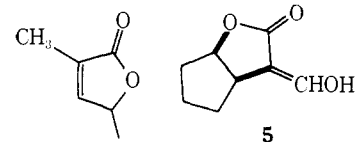
When **5** was treated with **9** (1.15 equiv) and K_2CO_3 (1.05 equiv, HMPA, 25°, 22 hr), a mixture of two diasteriomeric products was obtained (**10**, *ca.* 90%).[10]



1. R_1 = OH; R_2 = H
2, R_1 = H; R_2 = OH

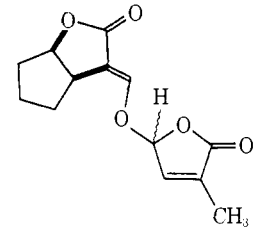


3, R_1 = OH; R_2 = H
4, R_1 = H; R_2 = OH



5

7. X = OC_2H_5
8. X = OH
9. X = Br



10

The nmr spectrum of this mixture was in close agreement with strigol for all relevant proton signals including the

(1) C. E. Cook, L. P. Whichard, B. Turner, M. E. Wall, and G. H. Egley, *Science*, **154**, 1189 (1966).

(2) The absolute stereochemistry of strigol has not been determined, and the enantiomer represented in **1** has been chosen arbitrarily. All other structures are racemic and are illustrated by one enantiomer.

(3) C. E. Cook, L. P. Whichard, M. E. Wall, G. H. Egley, P. Coggon, P. A. Luhan, and A. T. McPhail, *J. Amer. Chem. Soc.*, **94**, 6198 (1972).

(4) B. Miller, H. Marquiles, T. Drabb, Jr., and R. Wayne, *Tetrahedron Lett.*, 3081, 3085 (1970).

(5) J. D. Fissekis and B. A. Markert, *J. Org. Chem.*, **31**, 2945 (1966).

(6) D. M. Burness, *J. Org. Chem.*, **21**, 102 (1956).

(7) F. Fariña and M. V. Martín, *An. Quim.*, **67**, 315 (1971).

(8) J. P. van der Merwe and C. F. Garbers, *J. S. Afr. Chem. Inst.*, **17**, 149 (1964).

(9) R. G. Weiss and E. I. Snyder, *J. Org. Chem.*, **36**, 403 (1971). See also I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. Ind. (London)*, 900 (1966); J. Hooz and S. S. H. Gilani, *Can. J. Chem.*, **46**, 86 (1968).

(10) Satisfactory infrared, nuclear magnetic resonance, ultraviolet, and mass spectral data were obtained.