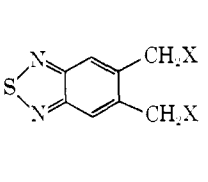
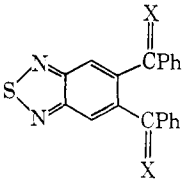
carbon tetrachloride gave the dibromide **10**, mp 109°, in 90% yield. Reaction of **10** with a slurry of aluminum chloride and benzene gave rise (80% yield) to the dibenzylthiadiazole **11**, mp 108°, which in turn was oxidized with sodium dichromate in acetic acid into the diketone **12** (mp 178°, 92% yield). Although attempts to convert this diketone directly into **4** have been unsuccessful, the heterocycle has been generated as a transient species by dehydration of its corresponding dihydrosulfoxide **13**. Sulfoxide **13** was prepared from the diketone **12** by sodium borohydride reduction of the latter. The resultant diol, **14**, was then converted with phosphorus pentasulfide into the sulfide **15** (mp 212°, 50% overall yield from **12**). Oxidation of **15** with *m*-chloroperbenzoic acid in chloroform solution gave the sulfoxide **13**, mp 250° dec, in 71% yield.

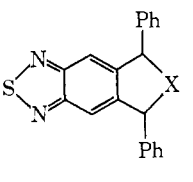
Upon heating 10^{-3} *M* solutions of sulfoxide **13** in acetic anhydride at 140°, a light blue color slowly formed. The visible spectrum of these solutions showed absorption at 645 nm, but all attempts to isolate heterocycle **4** from these reactions have resulted only in the high yield formation of an insoluble crystalline dimer, **16**. The infrared and ultraviolet spectra of **16**, mp >300°, show only the presence of a thiadiazole and thiophene ring system, indicating that dimerization of the heterocycle has occurred at the benzene ring and not at the thiophene ring.[7]



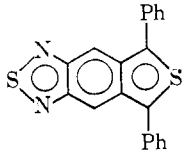
9, X = H
10, X = Br
11, X = Ph



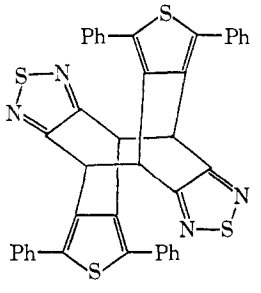
12, X = O
14, X = HOH



13, X = SO
15, X = S

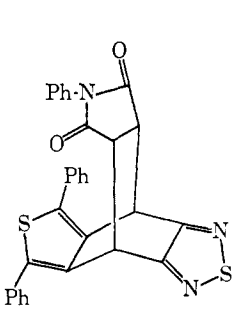


4

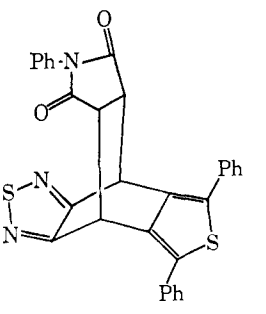


16

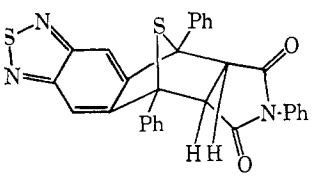
On the other hand, solutions of heterocycle **4** react with N-phenylmaleimide at both the benzene and thiophene rings, giving rise to adducts **17** (42% yield), **18** (24%), **19** (25%), and **20** (8%). Adducts **17** and **18** give absorption in the ultraviolet typical of thiadiazole and thiophene ring systems, while adducts **19** and **20** give absorption clearly indicating the presence of a benzothiadiazole residue. The assignment of *exo* geometry to **19** and *endo* geometry to **20** follows from the chemical shifts found for the protons α to the imide carbonyl groups in these adducts. Thus, singlet resonance at δ 5.1 was observed for adduct **19** while adduct **20** exhibited resonance at δ 4.15.[5] The nmr spectra of adduct **17**, mp 270°, and adduct **18**, mp 320°, are quite similar, and the configurational assignment indicated for these adducts must be considered uncertain.[9]



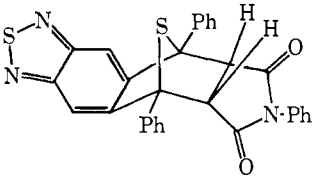
17



18



19



20

Further work on the preparation of a stable analog **4** along with a detailed chemical and theoretical investigation of these heterocyclic systems is in progress.

Acknowledgment. We wish to thank the National Science Foundation for funds to purchase the Hitachi mass spectrometer.

(9) Both adducts **17** and **18** show resonance for the protons α to the imide carbonyl groups at δ 3.7 and resonance for the bridgehead protons at δ 5.6.

J. D. Bower, R. H. Schlessinger
Department of Chemistry, University of Rochester
Rochester, New York 14627
Received September 30, 1969

The Stereochemistry of the Methylene Iodide–Zinc–Copper Couple Methylenation of Cyclic Allylic Alcohols[1]

Sir:

The reaction developed by Simmons and Smith[2] for methylene addition to double bonds has found wide application in organic synthesis. One of the more valuable aspects of this reaction is the stereochemical control exerted on the developing cyclopropane ring by a properly oriented hydroxyl group. First discovered by Winstein and coworkers[3] and later verified in a wide variety of simple systems,[4] the ability of a hydroxyl group to control the steric course of methylene addition has been successfully employed in several synthetic sequences.[5] Complex formation between the oxygen atom and the

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

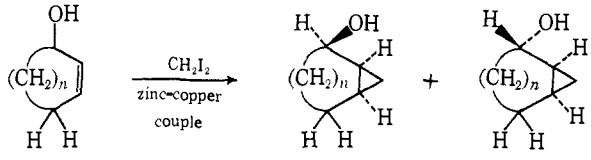
(2) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958).

(3) (a) S. Winstein, J. Sonnenberg, and L. de Vries, *ibid.*, **81**, 6523 (1959); (b) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961).

(4) (a) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963); (b) E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963); (c) A. C. Cope, S. Moon, and C. H. Park, *ibid.*, **84**, 4843 (1962); (d) J. J. Sims, *J. Org. Chem.*, **32**, 1751 (1967); (e) J. H. Chan and B. Rickborn, *J. Am. Chem. Soc.*, **90**, 6406 (1968).

(5) (a) W. G. Dauben and A. C. Ashcraft, *ibid.*, **85**, 3673 (1963); (b) P. Radlick and S. Winstein, *ibid.*, **86**, 1866 (1964); (c) R. Ginsig and A. D. Cross, *ibid.*, **87**, 4629 (1965); (d) M. Gasic, D. Whalen, B. Johnson, and S. Winstein, *ibid.*, **89**, 6382 (1967); (e) D. Whalen, M. Gasic, B. Johnson, H. Jones, and S. Winstein, *ibid.*, **89**, 6384 (1967).

organozinc reagent, followed by methylene transfer to the double bond, has been proposed[3b,4a,e] to account for the stereoselectivity and the large rate enhancement found for methylene addition to allylic alcohols relative to simple olefins. Based on a limited number of allylic and homoallylic alcohols, the hydroxyl group was proposed to exert a "*cis* directive influence"[4e] during cyclopropanation. However, preferential *anti* addition had already been reported in some larger, relatively complicated cyclic molecules.[5d,e] We have now reexamined the steric course of methylene addition to the cyclic allylic alcohols **1a–c** and extended the series to include **1d** and **1e**. In the latter systems the hydroxyl group is a highly selective *anti* director.



1a, $n = 1$ — **2a–e** (*syn*) — **3a–e** (*anti*)
b, $n = 2$
c, $n = 3$
d, $n = 4$
e, $n = 5$

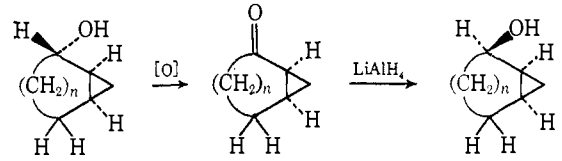
Organozinc reagent was generated from methylene iodide and zinc–copper couple,[3b] and reaction of the reagent with allylic alcohols **1a–e**[6] was followed by glpc.[9] Methylene addition was usually complete within 15–30 min; longer exposure to the organozinc reagent resulted in decreased yields of bicyclic products. The experimental results are summarized in Table I.

Table I. Product Distribution and Isolated Yields of **2** and **3**

Allylic alcohol	Epimer distribution[a] % **2** (*syn*)	% **3** (*anti*)	Isolated yield % (**2** + **3**)
1a	>99[b]		67
1b	>99[c]		71
1c	90[d]	10[d]	82
1d	0.5	99.5	74
1e	0.05	99.95	66

[a] Determined from analytical samples before bulk purification; control experiments indicated that epimer fractionation did not occur during work-up of the analytical samples. [b] Previously reported[4b] to be 98%. [c] Previously reported[4a] to be 100%; we could detect no **3b** in the mixture. [d] Previously reported[4c] to be 91% **2c** and 9% **3c**.

As previously reported,[4a–c] *syn* addition predominated for allylic alcohols **1a–c**.[10] However, treatment of **1d** and **1e** with organozinc reagent gave *anti* alcohols **3d** and **3e** (mp 54.5–55.5°), respectively.[11] The reactions were highly stereoselective; **3d** was contaminated with only 0.5% of its syn epimer (**2d**), and **3e** was contaminated by only 0.05% of **2e**.[12] Jones oxidation[13] of **3d** and **3e** followed by reduction of ketones **4d** and **4e** with

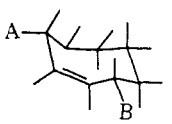


3d, e — **4d, e** — **2d, e**

lithium aluminum hydride gave *syn* alcohols **2d** and **2e**, contaminated with *ca.* 1% of the corresponding *anti* epimers. The relative configurations of **2d** and **2e** and **3d** and **3e** were assigned from the expected direction of hydride reduction of **4d** and **4e** and by comparing ir and nmr spectra of each epimeric pair. Models of ketones **4d** and **4e** suggest that hydride attack at the less hindered face of the carbonyl group would give the *syn* epimers. The hydroxyl groups of *syn* alcohols **2d** and **2e** must assume a hindered *endo* orientation with respect to the larger ring, while those of *anti* epimers **3d** and **3e** are oriented *exo* to the larger ring. The hydroxyl groups of the more hindered *syn* alcohols should be less available for intermolecular hydrogen bonding.[14] Our assignments are in agreement with the fact that the ir bands for the free hydroxyl stretch in **2d** (3600 cm^{-1}) and **2e** (3610 cm^{-1}) are significantly more intense than the corresponding bands for **3d** (3620 cm^{-1}) and **3e** (3630 cm^{-1}). In addition, the protons α to the hydroxyl substituent are deshielded by more than 1 ppm in **2d** (4.30 ppm) and **2e** (4.35 ppm) relative to *anti* alcohols **3d** (3.02 ppm) and **3e** (3.26) ppm,[15] in accord with the expected influence of a neighboring cyclopropane ring.[16]

From the data presented in Table I, it is evident that the transfer of methylene from the organozinc reagent to the double bonds of allylic alcohols **1a–e** is highly selective. Also, the direction of methylene addition changes from *syn* to *anti* between cyclohexen-3-ol (**1b**) and cyclooctene-3-ol (**1d**).[17] Models of **1b** indicate that the allylic hydroxyl group can only function as a *syn* director;[21] however, models of **1c** are less helpful in determining which face of the double bond is more accessable. In fact, the energy difference between *syn* and *anti* transition states giving **2c** and **3c** is only 1.3 kcal/mole. The abrupt switch from *syn* to *anti* direction as the ring size is increased from $n = 3$ to $n = 4$ is consistent with previous explanations for stereoselectivity[3b,4a,e] during methylene addition to allylic alcohols. One need only propose that the complexed organozinc reagent attacks the nearest face of the neighboring double bond. Anet and St. Jacques[22] suggested that cyclooctene preferred a chair–boat conformation; by analogy, the bulky hy-

(6) Only the *cis* isomers of **1d**[7] and **1e**[8] were studied.
(7) N. Heap and G. H. Whitham, *J. Chem. Soc., B*, 164 (1966).
(8) M. Santelli, M. Bertrand, and M. Ronco, *Bull. Soc. Chim. Fr.*, 3273 (1964).
(9) A 10 ft × 1/8 in. 5% Carbowax 20M column cleanly separated the components of the reaction mixtures.
(10) The properties of **2a–c** and **3c** agreed with those previously reported.
(11) All new compounds gave satisfactory elemental analyses; satisfactory ir and nmr spectra were also obtained.
(12) The identity of both minor epimers was established by coinjection with authentic samples on Carbowax 20M and DEGS.
(13) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).
(14) A. C. Cope, S. Moon, and P. E. Peterson, *J. Am. Chem. Soc.*, **84**, 1935 (1962).
(15) Chemical shifts are reported in δ (ppm) downfield from tetramethylsilane internal standard.
(16) R. S. Boikess, J. I. Brauman, and S. Winstein, unpublished work.
(17) Epoxidation of cyclic allylic alcohols is also selective. Treatment of **1b**,[18] **1c**,[19] and **1d**[20] with peracids gave the corresponding epoxides, and the stereoselectivity of oxygen addition parallels that of methylene addition with organozinc reagent. The hydroxyl group is thought to influence the stereoselectivity of epoxidation.
(18) H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1958 (1957).
(19) A. C. Cope, J. K. Heeren, and V. Seeman, *J. Org. Chem.*, **28**, 516 (1963).
(20) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, *J. Am. Chem. Soc.*, **79**, 3900 (1957).
(21) Rickborn and Chan[4e] suggest that 2 moles of organozinc reagent may be required in the transition state for methylene transfer; however, the *anti* direction is still geometrically unfavorable.
(22) M. St. Jacques, Ph.D. Dissertation, University of California, Los Angeles, 1967.



chair-boat

droxyl group, complexed with the organozinc reagent, should prefer an equatorial orientation (A or B). In either position, the relative location of the double bond and the hydroxyl group favors *anti* addition of methylene. Transannular hydrogen atoms shield the other side of the double bond; however, shielding does not dominate in the control of stereoselectivity since the allylic hydroxyl group appears to accelerate methylene addition. An examination of models also suggests that the relative orientation of the double bond and hydroxyl group in cyclononen-3-ol (**1e**) is similar to that for **1d**, which favors *anti* addition.

In summary, the stereoselectivity found for methylene addition to allylic alcohols by treatment with organozinc reagent can best be explained by assuming complexation between the hydroxyl group and the reagent, followed by methylene transfer to the nearest face of the double bond. In addition, the ease with which **2d**, **2e**, **3d**, and **3e** can be prepared epimerically pure, coupled with the stereoselectivity found in their homoallylic ring expansions,[5d,e,23] offers a convenient tool for the stereoselective synthesis of double bonds in medium rings.

(23) C. D. Poulter, E. C. Friedrich, and S. Winstein, unpublished work.

(24) National Institutes of Health Postdoctoral Fellow, 1967–1969.

C. Dale Poulter,[24] Edwin C. Friedrich, S. Winstein

Contribution No. 2451, Department of Chemistry
University of California, Los Angeles, California 90024

Received August 16, 1969

Book Reviews

Excitons in Molecular Crystals. Theory and Applications. By D. P. Craig and S. H. Walmsley, University College, London. W. A. Benjamin, Inc., 2 Park Ave., New York, N. Y. 1968. xi + 172 pp. 16 × 23.5 cm. $12.95.

Despite the heroic efforts of various workers, there exists a dichotomy in the theory of excitons in molecular crystals. For the spectroscopist, it usually means coherence, group theory, and Davydov splitting. For the specialist in exciton dynamics, it usually means incoherence, random walk, and Förster's resonance-transfer mechanism. In many areas of chemistry and physics two extreme models for related phenomena in different systems may coexist peacefully, but here the remarkable fact is that both models are used to explain different manifestations of the same thing... to take a common example, the lowest excited electronic state of crystalline anthracene. It seems clear that coherence prevails in the early life of the exciton, at least over a sufficient spatial volume to ensure observation of Davydov splitting, but as lattice scattering progresses, the exciton becomes localized and its motion incoherent. Fascinating events in this latter stage have been observed in recent years, collisions between triplet excitons and fission of singlet excitons into triplets being the best known.

Craig and Walmsley expose the theory of *coherent* exciton states in a readable manner. The prototype theory (of electronic resonance between two helium atoms), the necessary space group theory, and the essential complications due to vibrational modes are all developed clearly (if compactly) as befits the stated purpose of providing an introduction for seniors and young graduate students.

The publication of this book automatically invites comparison with A. S. Davydov's "Theory of Molecular Excitons," McGraw-Hill Book Co., New York, N. Y., 1962, translated by M. Kasha and M. Oppenheimer, Jr.; they are nearly identical in subject material, title, and size. They are found also to be identical in philosophy. Although more pedagogical and more up-to-date than the Davydov translation, Craig and Walmsley's book is still written primarily for the spectroscopist, with no theoretical development of exciton dynamics on the "hopping" model whatsoever. Particularly telling is the fact that Förster's fundamental paper appears nowhere among the references. As a consequence, the level and nature of the present understanding of many important dynamical exciton processes is not accurately represented. Bearing this carefully in mind, the prospective student of molecular excitons will benefit from the book.

R. S. Knox

Department of Physics and Astronomy
University of Rochester, Rochester, New York