

for the same reason. (c) Excitation of a square-planar complex to the  ${}^3E_g$  level makes the reaction allowed.

Thus, neither square-planar isomerization nor tetrahedral racemization are thermally allowed processes, if the mechanism involves a tetrahedral-square-planar interconversion. Photochemical *cis-trans* isomerization can, on the other hand, be allowed, in agreement with experiment.<sup>9-11</sup> Similar treatment of axial-equatorial interchange of the ligands of a trigonal-bipyramidal complex (through an intermediate or transition state with square-pyramidal geometry) shows that this reaction is, in agreement with Eaton's results, allowed, as is the substitution of square-planar complexes. Tetrahedral substitution is disallowed, in contrast to the results of the one-electron picture.<sup>12</sup> For a  $d^3$  complex, racemization by way of a Bailar twist<sup>13</sup> is thermally allowed for weak ligand fields, but disallowed for strong fields. The same result is obtained for other mechanisms proposed for this reaction.<sup>14, 15</sup>

Experimentally, there is little correlation between these predictions and observed reaction rates. This observation is hardly surprising, since the theory explicitly *ignores* changes in energy of the bonding levels of the complex.<sup>16</sup> The Woodward-Hoffmann treatment depends on the general assumption that if a reaction  $A \rightarrow B$  can occur by two pathways, then, *other factors being equal*, the allowed pathway will have the lower activation energy. Implicit in this statement is the necessity for a comparison between two modes of reaction. For systems containing only carbon atoms, the energy difference between the two pathways appears, at least in one case, to be quite large,<sup>17</sup> but this empirical observation is not guaranteed by the qualitative arguments of the theory. Unfortunately, in the reactions of transition metal complexes, distinguishable pathways for the same reaction are usually not available, and the "allowedness" or "disallowedness" of any single reaction is not experimentally defined. In many of the reactions considered here (and particularly in substitution reactions), the rate will be determined by changes in binding energies, in over-all ligand field stabilization, and in the strengths of bonds being made or broken during the reaction. The contribution of orbital symmetry conservation might be expected to be much smaller.

Thus, orbital symmetry arguments concerning reactions of transition elements must be viewed with caution. The qualitative theory described herein may be useful in rationalizing differences in thermal and photochemical behavior of a complex with regard to the same reaction, or in the comparison of two distinguish-

able paths from the same starting material to slightly different products, if appropriate experiments can be devised. Verification of this limited theory is being sought.

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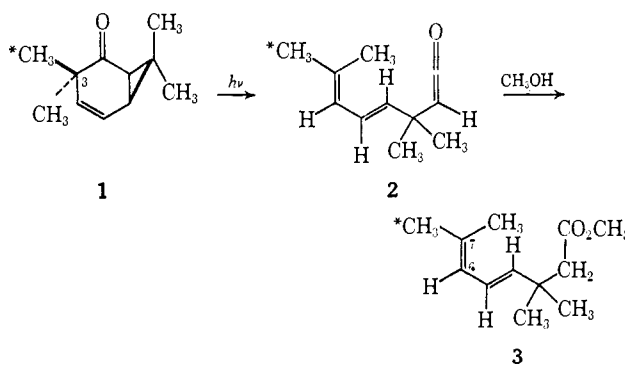
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### Stereoselective Photochemical Electrocyclic Valence Isomerization of 3-Methylcar-4-en-2-one

Sir:

One possible determinant of stereochemical selectivity in photochemical electrocyclic valence isomerizations for which the Hoffmann-Woodward generalizations seem to provide no unique predictions would be the ground-state geometry of the reactants.<sup>1, 2</sup> The stereochemical outcome would be dictated by the conformation of the light-absorbing species, rather than by the character of the substituents on a terminus of the moiety suffering electrocyclic change. Even identical substituents, distinguishable only by geometrical disposition and an isotopic label, might retain stereochemical individuality during the conversion.

We now report discovery of such an example: the photochemical valence isomerization of 3-methylcar-4-en-2-one (**1**) in ether-methanol gives the *trans* isomer of methyl 3,3,7-trimethylocta-4,6-dienoate, and the 3-*endo*-methyl group of **1** becomes the 7-methyl *cis* to H-C(6) in **3**.



3-Methylcar-4-en-2-one prepared from eucarvone (2,6,6-trimethylcyclohepta-2,4-dienone) using sodium amide and methyl iodide<sup>3</sup> was photolyzed ( $\lambda > 300$  nm) in ether containing 1.6% methanol to give after chromatography on silica gel 61% methyl 3,3,7-trimethylocta-4,6-dienoate.<sup>4, 5</sup> Analysis of the nmr ab-

(1) J. E. Baldwin and M. C. McDaniel, *J. Am. Chem. Soc.*, **90**, 6118 (1968), and references cited.

(2) S. M. Krueger, J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *J. Chem. Soc., B*, in press.

(3) E. J. Corey and H. J. Burke, *J. Am. Chem. Soc.*, **78**, 174 (1956).

(4) Photolysis of **1** in a  $CH_2Cl_2$ -THF glass at liquid nitrogen temperatures generated the ketene intermediate **2** having a strong infrared absorption at  $2110\text{ cm}^{-1}$ . Even at room temperature in ether the ketene may be generated and observed, and its reaction with added

(9) P. Haake and T. A. Hylton, *J. Am. Chem. Soc.*, **84**, 3774 (1962).

(10) V. Balzani, V. Carassiti, L. Moggi, and F. Scandola, *Inorg. Chem.*, **4**, 1243 (1965); V. Balzani and V. Carassiti, *J. Phys. Chem.*, **72**, 383 (1968).

(11) J. R. Perumareddi and A. W. Adamson, *ibid.*, **72**, 414 (1968).

(12) Note that any reaction involving a change of spin multiplicity is disallowed in terms of the definition used here.

(13) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

(14) P. Ray and K. Z. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

(15) C. S. Springer and R. E. Sievers, *Inorg. Chem.*, **6**, 852 (1967).

(16) Inclusion of these levels (or unoccupied p levels) in the configurations shown in Figure 1 would not change the appearance of this diagram at all, since, after the ordering of levels has been decided on, it depends entirely on symmetry properties of the complex.

(17) J. I. Brauman and D. M. Golden, *J. Am. Chem. Soc.*, **90**, 1920 (1968).

sorptions for the three vinyl protons gave  $H_A$  5.50,  $H_B$  6.08,  $H_C$  5.67 ppm;  $J_{AB} = 15.2$ ,  $J_{BC} = 10.2$ ,  $J_{AC} = 0.3$  Hz, and thus clear evidence for *trans* stereochemistry about the C(4)–C(5) double bond.<sup>6</sup> That the *trans* isomer is a primary photoproduct was established by nmr analyses of reaction mixtures during photolyses.

The  $CH_3$ –C(3) absorptions at 1.07 and 1.02 ppm in ketone **1** were assigned to the *endo* and *exo* methyls, respectively, for the *endo* substituent is positioned near the plane of the adjacent carbonyl group. When eucarvone was alkylated with methyl- $d_3$  iodide, 3-methyl- $d_3$ -car-4-en-2-one was obtained with high stereoselectivity; it had a methyl singlet at 1.02 ppm and no absorption at 1.07 ppm, and was accordingly assigned the *endo*-3-methyl- $d_3$  configuration. The epimeric labeled analog was synthesized from labeled eucarvone. The methoxyimine derivative of eucarvone was treated with potassium *t*-butoxide in DMSO- $d_6$ -dioxane (1:1), hydrolyzed with a solution of hydrochloric and levulinic acids in acetone, and purified; the eucarvone obtained had 85% incorporation of deuterium in the vinyl methyl group, as well as some olefinic label. The derived *exo*-methyl- $d_3$ -carenone had the expected band in the nmr at 1.07 ppm.

The low-field vinyl methyl in the dienolate **3** was assigned to  $CH_3$  *trans* to H–C(6), for it would be preferentially deshielded by the unsaturated functionality of the molecule. The unlabeled ester **3** showed absorptions for the two vinyl methyls at 1.718 and 1.734 ppm (relative to internal TMS in  $CCl_4$  at 100 MHz, 50 Hz sweep width, simultaneous saturation of the H–C(6) absorption). The photoproduct derived from *endo*-3-methyl- $d_3$ -carenone gave a doublet ( $J = 1.4$  Hz) for the vinyl methyl group which collapsed to a sharp singlet at 1.732 ppm with double irradiation of the H–C(6) absorption. Under the same spectroscopic conditions, the ester produced from *exo*-3-methyl- $d_3$ -carenone had a peak at 1.712 ppm.<sup>7</sup> Thus the sequence **1**  $\rightarrow$  **2**  $\rightarrow$  **3** proceeds with high stereoselectivity, even though the two substituents on C(3) differ only in configurational disposition and isotopic identity!

That the stereochemistry of photochemical valence isomerizations in systems having dissimilar substituents on the termini of the electron system formally involved<sup>1,2,8,9</sup> may be controlled by geometrical aspects of the ground-state light-absorbing species is an attractive but unestablished hypothesis. The present work does exemplify and confirm the possibility of a highly stereoselective photolytic isomerization in a molecule having, at each electrocyclic terminus, substituents above and below the plane of the  $\pi$  electron

system which, save for configurational differences, are identical. Electronic effects dependent on different substituents above and below the plane are, therefore, not a prerequisite of high stereoselectivity in such reactions.

The *trans* stereochemistry of the C(4)–C(5) double bond in **3** and the sense of twist about C(3)–C(4) in **1** necessary to attain the conversion **1**  $\rightarrow$  **2** are consistent with a view of the isomerization as a concerted (2 + 2 + 2 + 2) cycloaddition proceeding in a *cis* or suprafacial fashion on each two-center unit:  $\pi_{C=O}$ ;  $\sigma_{C(2)-C(3)}$ ;  $\pi_{C(4)-C(5)}$ ;  $\sigma_{C(6)-C(1)}$ .<sup>10</sup> Alternative concerted mechanisms, based on nonconcerted models in which diradical intermediates are held to possess the requisite stereochemical preferences, are also formal possibilities.

**Acknowledgment.** This investigation was supported by Public Health Service Research Grant No. GM-14381 and GM-16576. The 100-MHz nmr spectra were recorded by Mr. Robert Thrift.

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

(11) Alfred P. Sloan Foundation Fellow; inquiries should be directed to the University of Oregon.

(12) University Fellow (1966–1967) and Sun Oil Fellow (1967), University of Illinois; National Institute of General Medical Sciences Predoctoral Fellow, 1968.

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## Synthesis of Methyl Stercolate<sup>1</sup>

Sir:

Being interested in the synthesis of cyclopropene acids such as sterculic acid (9,10-methano-9-octadecenoic acid),<sup>2</sup> we tried the reported seemingly straightforward Simmons–Smith addition of methylene to methyl stearolate.<sup>3</sup> In our hands this method failed to produce detectable amounts of cyclopropene material.<sup>4</sup> Diazomethane in the presence of cuprous chloride or bromide<sup>5</sup> likewise failed to convert methyl stearolate to methyl stercolate. We now wish to report a synthesis that effects this conversion in *ca.* 30% yield.

Diazoacetic ester in the presence of copper-bronze reacted with methyl stearolate (**1**) to give the diester<sup>6</sup> of cyclopropene diacid (**2**). The diacid itself, mp 24.5–26.0°, could be obtained in 60–70% conversion (70–90% yield) from stearolate. *Anal.* Calcd for  $C_{20}H_{34}O_4$ : C, 70.97; H, 10.12. Found: C, 71.20; H, 10.21.

(1) We acknowledge the support of the Southern Regional Research Laboratory, U. S. Department of Agriculture (Research Grant 12-14-100-7992(72)), that made this work possible, and thank the National Science Foundation for funds under Research Equipment Grant GP 3618 for the purchase of an nmr spectrophotometer.

(2) J. R. Nunn, *J. Chem. Soc.*, 313 (1952). Also see P. K. Faure and J. C. Smith, *ibid.*, 1818 (1956).

(3) N. C. Castellucci and C. E. Griffin, *J. Am. Chem. Soc.*, **82**, 4107 (1960).

(4) Others have tried this method also without success. Thus, note S. D. Andrews and J. C. Smith, *Chem. Ind. (London)*, 1636 (1966); A. R. Johnson, CSIRO, Australia, private communication.

(5) See R. E. Pincock and J. I. Wells, *J. Org. Chem.*, **29**, 965 (1964). Actually, attempts at adding methylene from diazomethane to stearolic acid had already been made, but with negative results [J. P. Varma, S. Dasgupta, B. Nath, and J. S. Aggarwal, *J. Indian Chem. Soc.*, **33**, 111 (1955); also see D. G. Brooke and J. C. Smith, ref 6].

(6) D. G. Brooke and J. C. Smith, *Chem. Ind. (London)*, 1508 (1957).

methanol followed. Compare O. L. Chapman and J. D. Lassila, *J. Am. Chem. Soc.*, **90**, 2449 (1968); L. Bacher, O. L. Chapman, and J. D. Lassila, *ibid.*, **90**, 5933 (1968).

(5) A. J. Bellamy and G. H. Whitman (*J. Chem. Soc.*, 4035 (1964)) photolyzed an ethereal solution of ketone **1** in the presence of cyclohexylamine and obtained N-cyclohexyl-3,3,7-trimethylocta-4,6-dienamide of unspecified stereochemistry.

(6) Compare the nmr data for the *trans* isomer of methyl 2,6-dimethylhepta-3,5-dienoate: P. M. Collins and H. Hart, *J. Chem. Soc.*, **C**, 1197 (1967).

(7) The very small apparent deuterium isotope effect on the chemical shift of the  $CH_3$ –C(7) protons is, as expected, to higher field, and of greater magnitude in the system having D–C(6) as well as CD<sub>3</sub>–C(7); cf. P. Laszlo and Z. Welvart, *Bull. Soc. Chim. France*, 2412 (1966).

(8) D. J. Patel and D. I. Schuster, *J. Amer. Chem. Soc.*, **90**, 5137 (1968).

(9) L. A. Paquette, R. F. Eizember, and O. Cox, *ibid.*, **90**, 5153 (1968).