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.[6] 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 dienoate **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.[7] Thus the sequence **1** → **2** → **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[1,2,8,9] 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 k 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** → **2** are consistent with a view of the isomerization as a concerted (2 + 2 + 2 + 2) cycloreaction proceeding in a *cis* or suprafacial fashion on each two-center unit: $\pi_{C=O}$; $\sigma_{C(2)-C(3)}$; $\pi_{C(4)-C(5)}$; $\sigma_{C(6)-C(1)}$.[10] Alternative conceptualizations, based on nonconcerted models in which diradical intermediates are held to possess the requisite stereochemical preferences, are also formal possibilities.

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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_3–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).

(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 Sterculate[1]

Sir:

Being interested in the synthesis of cyclopropene acids such as sterculic acid (9,10-methano-9-octadecenoic acid),[2] we tried the reported seemingly straightforward Simmons–Smith addition of methylene to methyl stearolate.[3] In our hands this method failed to produce detectable amounts of cyclopropene material.[4] Diazomethane in the presence of cuprous chloride or bromide[5] likewise failed to convert methyl stearolate to methyl sterculate. 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[6] 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.

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(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).

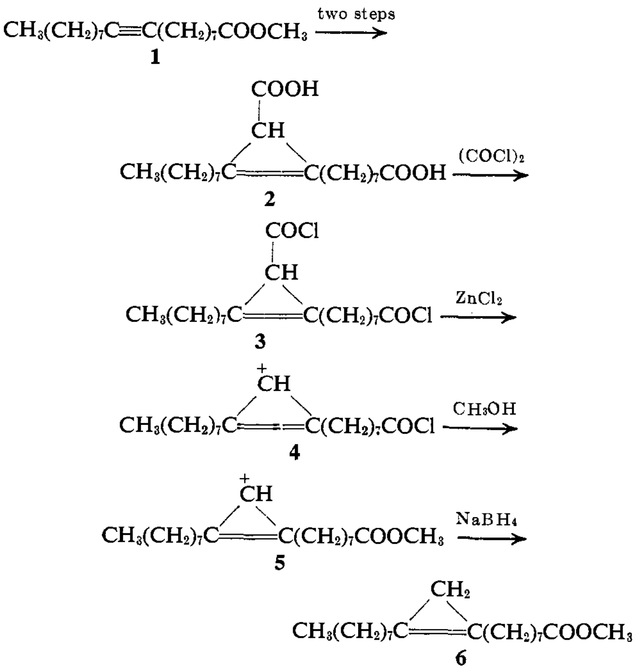
(3) N. C. Castellucci and C. E. Griffin, *J. Am. Chem. Soc.*, **82**, 4107 (1960).

(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 (1956); also see D. G. Brooke and J. C. Smith, ref 6].

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

Direct decarbonylation of cyclopropene acids such as in **2** to give the cyclopropenium ion is a known process.[7] However, to avoid using the potentially hazardous perchloric acid–acetic anhydride reagent we chose to operate *via* acid chloride **3**, which was obtained readily with excess oxalyl chloride. Treatment of diacid chloride **3** with zinc chloride selectively decarbonylated the chlorocarbonyl group in the cyclopropene ring to give **4** without affecting the second acid chloride grouping. Reaction with methanol converted the acid chloride, which is susceptible to borohydride reduction, to the ester **5**, which is not. The cyclopropenium ion ester **5** was then treated with sodium borohydride to reach the desired product, methyl sterculate (**6**), in 40% yield from diacid **2**.



Synthetic methyl sterculate [*Anal.* Calcd for $C_{20}H_{36}O_2$: C, 77.82; H, 11.76. Found: C, 77.83; H, 11.64] was obtained as a colorless oil sensitive to both heat and air. The material showed the expected features in its nmr and infrared absorption spectra, which were indistinguishable from those taken with pure methyl sterculate from *Sterculia foetida*.[8] The synthetic and natural materials gave single spots on thin-layer chromatographic plates, with the same R_f values. Gas–liquid partition chromatography with the two materials produced curves that were virtually superposable.[9,10] For further check on homogeneity and identity, the two materials were converted to their methylthiol adducts.[10,11] The adducts gave identical gas–liquid partition chromatography curves showing a single symmetrical peak. The infrared and the nmr absorption curves were also identical.

Work on the synthesis of ^{14}C-labeled malvalic acid (8,9-methano-8-heptadecenoic acid) is under way.

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[7] F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964); A. W. Krebs, *Angew. Chem.*, **77**, 10 (1965).

[8] We are indebted to Alan R. Johnson, Commonwealth Scientific and Industrial Research Organization, Ryde, Australia, for a sample of pure methyl sterculate isolated from *Sterculia foetida*.

[9] See A. C. Fogerty, A. R. Johnson, J. A. Pearson, and F. S. Shenstone, *J. Am. Oil Chemists' Soc.*, **42**, 885 (1965); F. G. Magne, *ibid.*, **42**, 332 (1965); H. W. Kircher, *ibid.*, **42**, 899 (1965).

[10] H. W. Kircher, *ibid.*, **41**, 4 (1964).

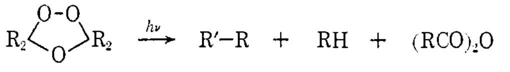
[11] P. K. Raju and R. Reiser, *Lipids*, **1**, 10 (1966); N. K. Hooper and J. H. Law, *J. Lipid Res.*, **9**, 270 (1968).

Photochemistry of Ozonides. Generation of Tetramethylcyclobutadiene in Photolysis of Hexamethyl Dewar Benzene Monoozonide

Sir:

Photodecomposition of hexamethyl Dewar benzene monoozonide (**1**) has been found to give tetramethylcyclobutadiene (**2**) as evidenced by the isolation of tetramethylcyclobutadiene dimer, *syn*-octamethyltricyclooctadiene (**3**). This rather remarkable reaction is one of two particularly instructive examples which were chosen for defining the scope and applicability of ozonide photolysis.[1,2]

Most ozonides have been found to photolyze according to the general scheme outlined in eq 1 in which a double *β* scission follows homolysis of the oxygen–oxygen bond. Cage recombination of the resulting carbon radicals is reasonably efficient.[1,2] The examples described in this preliminary report, hexamethyl Dewar benzene ozonide and diphenylacenaphthalene ozonide, are ones for which double *β* scission should lead to interesting but unstable products.



(1)

By analogy to our earlier observation that irradiation of cyclopentene ozonide (**5**) gives good yields of cyclopropane,[1,2] it was anticipated that hexamethyl Dewar benzene monoozonide (**1**) may yield tetramethylcyclobutadiene (**2**) as a transient intermediate. This expectation appears to have been borne out. Using conditions previously described,[1] we photolyzed **1**, mp 53–54,[3] in pentane and obtained *syn*-octamethyltricyclooctadiene (**3**)[4,5] in 19% yield, mp 196–198°, along with the ketone **4** in 30% yield; infrared (**4**) (CCl_4, cm^{-1}): 1700 (s), 1628 (s); nmr (CCl_4, δ): 1.25 (s), 1.75 (s), 2.00 (s), 3.53 (d), 3.85 (d), in the ratio 3:6:3:1:1; mass spectrum: *m/e* 150, 107, 43. Isolation of the dimer **3** does not, of course, unequivocally establish the intermediacy of **2**.

That the presumed intermediate cyclobutadiene **2** is singlet is supported both by the exclusive formation of *syn* dimer **3**[6–8] and by virtue of the nature of the reaction, which we believe may lead directly to singlet product. Cyclopentene ozonide (**5**), for example, gives no more than a trace, if any, of propane or propene,[1,2]

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[1] P. R. Story, W. H. Morrison, III, T. K. Hall, J-C. Farine, and C. E. Bishop, *Tetrahedron Letters*, 3291 (1968).

[2] P. R. Story, T. K. Hall, W. H. Morrison, III, and J-C. Farine, *ibid.*, 5397 (1968).

[3] H. Junker, W. Schafer, and H. Niedenbrück, *Chem. Ber.*, **100**, 2508 (1967).

[4] R. Criegee and G. Louis, *ibid.*, **90**, 417 (1957).

[5] R. Criegee, G. Schröder, G. Maier, and H-G. Fischer, *ibid.*, **93**, 1553 (1960).

[6] P. S. Skell and R. J. Peterson, *J. Am. Chem. Soc.*, **86**, 2530 (1964).

[7] L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965); **88**, 623 (1966).

[8] M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 3255 (1965).