The nmr data clearly indicate that $C_{3'}$, C_5, and the $C_{6'}$-methyl group are derived from the methyl group of acetate. The magnitude of the observed coupling constants is in accord with the degree of s character at these respective carbon atoms. These results from the ^{13}C study are in accord with the prior biogenetic study of griseofulvin employing the conventional ^{14}C-labeling method.[6]

The application of this ^{13}C method for the study of the biosynthesis of other microbial products is now in progress in this laboratory.

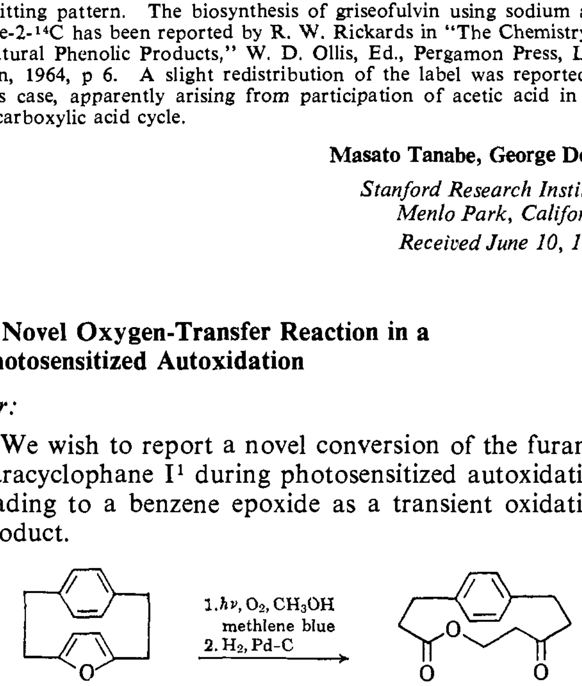
[6] A. J. Birch, R. A. Massy-Westropp, R. W. Richards, and H. Smith, *J. Chem. Soc.*, 360 (1958). In this study acetic acid-1-^{14}C was employed. We have made a similar study with sodium acetate-1-^{13}C; observations of the ^{13}C satellite bands of the $C_{6'}$–H in the griseofulvin obtained in this manner was precluded by the complexity of the $C_{6'}$–H splitting pattern. The biosynthesis of griseofulvin using sodium acetate-2-^{14}C has been reported by R. W. Rickards in "The Chemistry of Natural Phenolic Products," W. D. Ollis, Ed., Pergamon Press, London, 1964, p 6. A slight redistribution of the label was reported in this case, apparently arising from participation of acetic acid in the tricarboxylic acid cycle.

Masato Tanabe, George Detre
Stanford Research Institute
Menlo Park, California
Received June 10, 1966

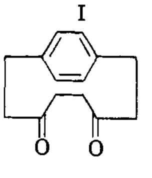
A Novel Oxygen-Transfer Reaction in a Photosensitized Autoxidation

Sir:

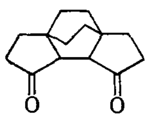
We wish to report a novel conversion of the furanoparacyclophane I[1] during photosensitized autoxidation leading to a benzene epoxide as a transient oxidation product.



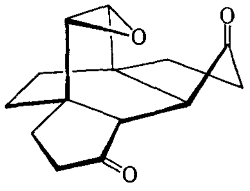
I II



III



IV



V

A methanolic solution of I was irradiated in the presence of methylene blue for 18 hr at 25° with a 150-w flood lamp while air was bubbled through the reaction medium. The solution was concentrated under reduced pressure and hydrogenated over palladium on charcoal for 24 hr.[2] Chromatography of the crude hydrogenated material over silica gel gave three products, A (26%), B (11%), and C (5%).

Compound A, mp 118–120°, was shown to be the keto lactone, II. *Anal.* Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.50; H, 6.93. The infrared spectrum ($CHCl_3$) shows strong absorption at 1725 (sh), 1710, and 1134 cm^{-1}. The nmr spectrum ($CDCl_3$) shows a singlet at τ 2.90 (4 H), triplets at 6.01 (2 H), 7.47 (4 H), and 8.02 (2 H), and a complex multiplet centered at 7.02 (4 H). Reduction of II to the triol with lithium aluminum hydride followed by tosylation and then further reduction with lithium aluminum hydride led to 1-propyl-4-amylbenzene. This product is identical with the hydrocarbon prepared by the Friedel–Crafts acylation of propylbenzene followed by Wolff–Kishner reduction. *Anal.* Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.85. Found: C, 88.50; H, 11.79. The mass spectrum shows a parent peak at m/e 190 and the expected peaks at m/e 133 and 161.

Compound B was shown to be identical with III (infrared, nmr, mixture melting point), a product previously prepared from I by Cram.[1]

Compound C, mp 145–147°, formed in low yield, was unstable to acid or base. *Anal.* Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94; mol wt, 232. Found: C, 72.21, 72.41; H, 6.93, 6.94; mol wt (mass spectrum), 232. While transparent in the ultraviolet, compound C shows peaks in the infrared at 1730 and 1245 cm^{-1} suggesting the presence of a five-membered ring ketone and an ether linkage. A most interesting feature of its structure, shown by the nmr spectrum, is the complete absence of all aromatic protons.

While the above spectroscopic data and our earlier work on the photooxidation of a related furanoheterocyclophane system[3] led us to believe that C contains the main structural features of IV, the final location of the ether oxygen in V and the stereochemistry of the molecule rest on the results of a single-crystal X-ray structure determination.

Compound C crystallizes in the monoclinic system, with cell dimensions a = 12.97, b = 11.03, c = 9.17 A, β = 117.98°, and four molecules in the unit cell. The observed and calculated densities are 1.32 and 1.33 g/cm^3, respectively. The systematic absences (hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$) are consistent with either of the space groups Cc or C2/c. Using a General Electric XRD-6 diffractometer equipped with single-crystal orienter and a balanced Ni–Co filter pair, three-dimensional intensity data were collected, by the stationary crystal–stationary counter method, to the limit $2\theta = 110°$; orienter settings were computed using λ 1.5405 A (Cu Kα_1). Due to rather poor crystal quality, only 683 of the 861 possible independent reflections were considered to have observable intensity.

The usual correction factors were applied to produce a set of structure amplitudes ($|F|$) from the intensity data. These structure amplitudes were then converted by use of a K(s) curve[4] to normalized structure amplitudes ($|E|$). The statistical averages[5] (Table I) and distributions[5] (Table II) of the normalized structure factors imply that the crystal is centrosymmetric and that the correct space group is C2/c. Since this space group has eightfold general multiplicity and the unit cell contains only four molecules, the molecule must be centered at a twofold symmetry position (*i.e.*, an inversion center or a twofold rotation axis). Each asymmetric unit of the cell, therefore, contains one-half a chemical molecule, or $^1/_2(C_{14}H_{16}O_3)$. Since the mole-

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[1] D. J. Cram and G. R. Knox, *J. Am. Chem. Soc.*, **83**, 2204 (1961); D. J. Cram, C. S. Montgomery, and G. R. Knox, *ibid.*, **88**, 515 (1966).

[2] The unhydrogenated reaction mixture tended to decompose rapidly on work-up, giving polymeric material.

[3] H. H. Wasserman and A. R. Doumaux, *J. Am. Chem. Soc.*, **84**, 4611 (1962).

[4] J. Karle and H. Hauptman, *Acta Cryst.*, **6**, 473 (1953).

[5] Theoretical values as recorded in I. L. Karle, K. S. Dragonette, and S. A. Brenner, *ibid.*, **19**, 713 (1965).

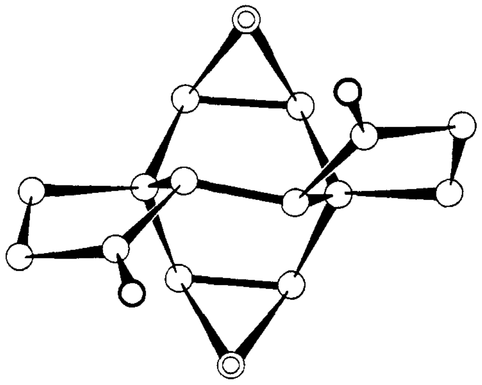


Figure 1. View of the crystallographic "molecule" along the twofold rotation axis. Carbon atoms are represented by single circles, carbonyl oxygen atoms by heavy circles, and the disordered ether oxygen "half-atoms" by double circles.

cule has an odd number of oxygen atoms, at least one of these must be either (1) located on a symmetry axis or point, or (2) orientationally disordered.

Table I

	Experimental	Theoretical Centro-symmetric	Noncentro-symmetric
$\langle\|E\|\rangle$	0.797	0.798	0.886
$\langle\|E^2 - 1\|\rangle$	0.962	0.968	0.736
$\langle\|E\|^2\rangle$	0.975	1.000	1.000

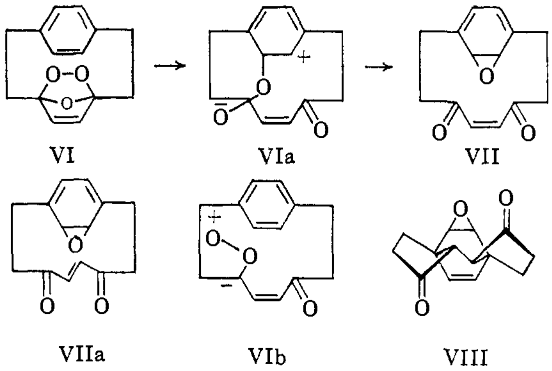
Table II

	Experimental, %	Theoretical, % Centro-symmetric	Noncentro-symmetric
$\|E\| > 3$	0.5	0.3	0.01
$\|E\| > 2$	3.8	5.0	1.8
$\|E\| > 1$	28.6	32.0	37.0

By use of the technique of symbolic addition,[6] it was possible to deduce, in terms of three symbolic letter phases, the signs of 76 reflections with large $|E|$ values. The map computed as the sum of a Fourier series with one of these letter combinations clearly showed a skeleton corresponding to IV centered on a crystallographic twofold rotation axis. An electron density map obtained by assigning the phases corresponding to this skeleton to the observed structure amplitudes showed a peak in the proper location for the ether oxygen of V. The structure has been refined, assuming a twofold disordered structure, to an R value of 0.195 using the block diagonal approximation to the least-squares method.

Figure 1 shows a view of this crystallographic "molecule" parallel to the twofold rotation axis. The ether oxygen is presumably in either one or the other of the two indicated positions in any individual chemical molecule; it appears as 0.5 oxygen in the electron density map, which can give only the position average of a large number of molecules. Because of this disorder, the standard deviations in the coordinates of the ether oxygen are considerably higher than those for the other atoms, but the present stage of the refinement[7] establishes the structure and stereochemistry of compound C as V.

We have suggested a mechanism for the formation of V from I: (i) the intermediate *endo*-peroxide (VI) breaks down to the transient benzene epoxide VII by an intramolecular transfer of oxygen through VIa (or possibly by electrophilic substitution involving a species such as VIb); (ii) isomerization of VII to VIIa[8] followed by intramolecular Diels–Alder reaction leads to VIII, which is hydrogenated to V.



Acknowledgment. This work was supported in part by U. S. Public Health Service Grant GM 13854-01.

Harry H. Wasserman, Arthur R. Doumaux[9]
Department of Chemistry, Yale University
New Haven, Connecticut

Raymond E. Davis
Center for Crystallographic Research
Roswell Park Memorial Institute, Buffalo, New York

Received August 8, 1966

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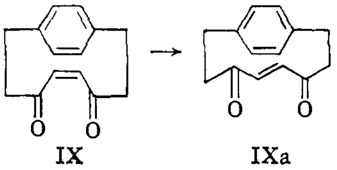
[6] I. L. Karle and J. Karle, *Acta. Cryst.*, **16**, 969 (1963). The computer program SORTE, written by A. Bednowitz, was used to facilitate application of the method.

[7] Attempts were made to refine an ordered structure in the lower symmetry space group Cc, but these also indicated the presence of only 0.5 oxygen at each of the possible ether oxygen positions. In addition, molecular dimensions were considerably less satisfactory, probably due to the more unfavorable observation:parameter ratio. Further refinement of the structure is in progress, as well as attempts to grow more satisfactory crystals, so that the nature of the disorder can be investigated further.

[8] We have observed that isomerization of the related *cis*-enedione (IX) to the *trans* form (IXa) takes place under the reaction conditions employed in the present work.



[9] National Institutes of Health Predoctoral Fellow, 1962–1966.

Decomposition of N-Nitrosohydroxylamine Derivatives

Sir:

Studies of the decompositions of organic acyl peroxides have contributed much to our present understanding of the chemistry of organic radical species.[1] We presently wish to report the preliminary results of

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[1] (a) W. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966; (b) J. O. Edwards, "Peroxide Reaction Mechanisms," John Wiley and Sons, Inc., New York, N. Y., 1962; (c) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.