an infrared spectrum indistinguishable from those of authentic *all-trans*-geranylgeraniol. The nmr, mass spectrometric, and chromatographic data thus establish the principal esterifying alcohol in bacteriochlorophyll from *R. rubrum* as *all-trans*-geranylgeraniol. The corresponding alcohol from the fully deuterated bacteriochlorophyll is, therefore, fully deuterated geranylgeraniol. These findings are entirely compatible with the suggestion that geranylgeraniol pyrophosphate may be a precursor in the biosynthesis of phytol.[6]

It is now necessary to indicate the nature of the esterifying alcohol in naming the bacteriochlorophylls, and we have found it convenient to designate them bacteriochlorophyll (gg) and bacteriochlorophyll (phy). It should be noted that Wellburn has esterified chlorophyll a with geranylgeraniol by an *in vitro* enzymatic transesterification.[7] This product was called chlorophyll a (gg).

The observations reported here have obvious implications concerning photosynthesis, lipid and carotenoid metabolism, and the taxonomy of purple photosynthetic bacteria.[8]

Acknowledgment. Our interest in the bacteriochlorophylls[3] was stimulated by a report presented by Drs. David H. Dolphin and A. Gomez-Revilla at a meeting on the "Primary Photochemistry of Photosynthesis" held at Argonne National Laboratory in Nov 1971. At that time, Dr. Dolphin announced that the esterifying alcohol in bacteriochlorophyll from *R. rubrum* was not the expected phytol. Subsequent work at Argonne National Laboratory, reported here, establishes the identity of this alcohol. We thank Dr. Dolphin for reading our manuscript and for a sample of pure *all-trans*-farnesol. We are also deeply grateful to Drs. H. Rilling and L. Altman for a very pure sample of *all-trans*-geranylgeraniol.

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(6) A. R. Wellburn, K. J. Stone, and F. W. Hemming, *Biochem. J.*, **100**, 23C (1966).

(7) A. R. Wellburn, *Phytochemistry*, **9**, 2311 (1970).

(8) NOTE ADDED IN PROOF. H. Brockmann, Jr., and G. Knobloch (*Arch. Mikrobiol.*, **85**, 123 (1972)) have just published the finding that *R. rubrum* bacteriochlorophyll is a farnesyl ester. As no experimental data are given about either the nmr or mass spectroscopy on which the identification of Brockmann and Knobloch is based, the possibility that the esterifying alcohol in *R. rubrum* bacteriochlorophyll is strain dependent remains. We are investigating this possibility.

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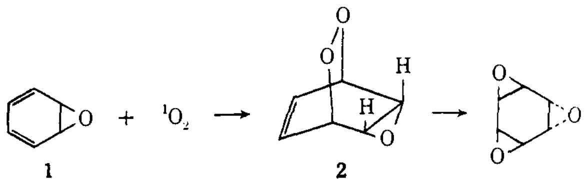
Synthesis of *trans*-Benzene Trioxide

Sir:

We wish to report a unique synthesis of *trans*-3,6,9-trioxatetracyclo[6.1.0.0^{2,4}.0^{5,7}]nonane (**3**) by thermal rearrangement of the 1,4-*endo*-peroxide (**2**) obtained from addition of singlet oxygen to oxepin—benzene oxide (**1**).



1 **2** **3**

Reaction of **1**[1] with singlet oxygen generated from hypochlorite–hydrogen peroxide by the method of Foote,[2] extraction with ether, and evaporation yielded a semicrystalline residue that, on addition of a small amount of ether, gave 37% of pure, crystalline **2**.[3,4] The mass spectrum[5] of **2** shows a parent peak at *m/e* 126, the base peak at *m/e* 94 due to loss of O_2 from the molecular ion, and a peak at *m/e* 66 (relative intensity 42%) due to subsequent loss of CO.

Peroxide **2** undergoes *quantitative* rearrangement to **3**[3,6] in $CHCl_3$ at 45° with a half-life for the reaction of approximately 14 hr. The facile rearrangement of **2** to **3** is particularly interesting in view of the previously reported rearrangements of 1,4-*endo*-peroxides derived from 1,3-cyclohexadienes that require higher temperature and yield mixtures of hydroxy ketone or epoxy ketone in addition to bisepoxide.[7] The nmr spectrum of **3**[6] establishes that one epoxy group is trans to the other two epoxy groups and, consequently, establishes that the epoxy group and the endoperoxy group in **2** are trans.

endo-Peroxide **2** can also be prepared from the reaction of **1** with singlet oxygen generated from the adduct of ozone and triphenyl phosphite.[8] Attempts to prepare **2** by photosensitized oxygenation of **1** with Methylene Blue as sensitizer gave mainly phenol.

Further studies of **2** and **3** will be described at a later date.

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(2) C. S. Foote, *et al.*, *J. Amer. Chem. Soc.*, **90**, 975 (1968).

(3) Satisfactory elemental analyses have been obtained for **2** and **3**.

(4) Mp 91–92°; ir ($CHCl_3$) 3015, 1405, 1372, 1285, 973, 920, 882, and 847 cm^{-1}; nmr ($CDCl_3$) δ 3.75 (2 H, m, epoxy H), 5.1 (2 H, m, bridgehead H), and 6.35 ppm (2 H, t, $J = 4$ Hz, olefinic H).

(5) Direct inlet, source temperature <100°; we thank Mr. John Dolhun for the mass spectra.

(6) Mp 84–86°; ir ($CHCl_3$) 3020, 1450, 1239, 950, and 860 cm^{-1}; nmr ($CDCl_3$) δ 3.4 (4 H, s) and 3.5 ppm (2 H, s); mass spectrum[5] (70 eV) *m/e* (relative intensity) 126 (M, 5), 97 (26), 81 (21), 71 (52), 69 (75), 68 (61), 43 (22), 42 (21), 41 (100), and 39 (55).

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