

mA and the reaction was terminated. The sulfur dioxide was allowed to evaporate and the ether soluble products were chromatographed on silica gel. Starting material (100 mg), 1,2,3-triphenyl-1-methoxyindene (II) (100 mg), and an unidentified methoxylated product (III) were successively eluted.⁶ The rearranged product II was identified by nmr, ir, uv, and mp comparison with material synthesized from 2,3-diphenylindenone and phenylmagnesium bromide followed by methanol-H₂SO₄.⁷ Product III apparently results from electrooxidation of II since III is the sole product of the independent oxidation of II at 1.2 V in sulfur dioxide-0.033 M methanol.

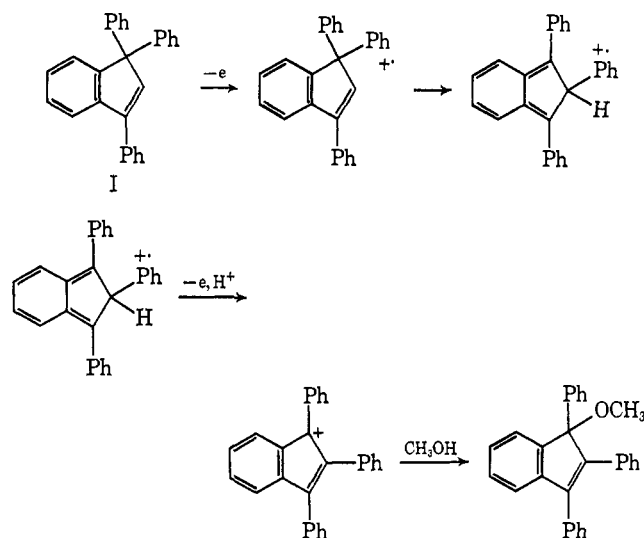
Cyclic voltammetric studies of 0.0027 M 1,1,3-triphenylindene and of II gave irreversible peaks at $E_p = 1.35$ and 1.1 V, respectively, in sulfur dioxide-tetrabutylammonium perchlorate. Addition of methanol (0.033 M) changed the height and shape of the anodic peak slightly, but since methanol does not oxidize appreciably at 1.4 V, this appears to be due to changed follow-up reactions. Since the rearrangement is triggered by electron transfer from triphenylindene it is possible that we have discovered the sought-after sigmatropic cation radical reaction. Other acceptable mechanisms can, however, be proposed so that an accurate elucidation of the nature of this process must await further study. It will be especially interesting to establish the reason(s) for the survival of II when macrooxidizing I, since II has a lower E_p than I. This appears to be due to the low solubility of II.

Electrooxidation of I in methanol-lithium perchlorate at platinum gave two methoxy products. One has been identified as 1,1,3-triphenyl-2,3-dimethoxyindane by its nmr and mass spectra, microanalysis, and conversion to 2-methoxy-1,1,3-triphenylindene in acid.⁸ The other product is a dimer which has not been fully characterized. The rearranged product, II, was absent indicating that the use of the nonnucleophilic solvent, sulfur dioxide, is necessary to avoid trapping before rearrangement. The use of sulfur dioxide could be of general importance in reactions where solvent trapping needs to be avoided. Dimerization and frag-

(6) Anodic "passivation" apparently prevents total oxidation of I and II. Wiping the anode clean will allow momentary restoration of relatively high currents in either I or II oxidation, but it is not possible to carry the reactions to completion.

(7) C. F. Koelsch and R. V. White, *J. Org. Chem.*, **6**, 602 (1941); E. P. Kohler and W. E. Mydans, *J. Amer. Chem. Soc.*, **54**, 4667 (1932).

(8) The oxidation of indene at platinum in methanol has been reported by H. Schafer and E. Steckhan, *Angew. Chem., Int. Ed. Engl.*, **8**, 518 (1969).



mentation as well as rearrangement reactions are cases to be considered.

Previous reports on the use of sulfur dioxide as an electrochemical solvent are apparently limited to a series of papers by Elving and coworkers who could find no fully satisfactory background electrolytes.⁹ We find the resistance of tetrabutylammonium perchlorate and other tetraalkylammonium salts to be sufficiently low to do macroscale oxidations as well as voltammetry.¹⁰ At -22° tetrabutylammonium perchlorate (0.2 M) and tetrapropylammonium hexafluorophosphate (0.2 M) have conductivities of 9×10^{-8} ohm⁻¹ cm⁻¹. Such solutions have a very large anodic potential range and have been utilized for several electrosyntheses in which nucleophilic trapping by solvent was to be avoided. The unreactivity of sulfur dioxide-tetrabutylammonium perchlorate toward cation radicals was further illustrated by oxidizing 9,10-diphenylanthracene.¹¹ The cyclic voltammogram demonstrated the stability of the cation radical at sweep rates as low as 0.06 V/sec.

(9) D. A. Hall, M. Sakuma, and P. J. Elving, *Electrochim. Acta*, **11**, 337 (1966).

(10) The utility of sulfur dioxide was suggested by Dr. A. Kentaro Hoffman.

(11) J. Phelps, K. S. V. Santhanam, and A. J. Bard, *J. Amer. Chem. Soc.*, **89**, 1752 (1967).

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Book Reviews

Annual Survey of Photochemistry. Volume 1. Survey of 1967 Literature. By NICHOLAS J. TURRO, GEORGE S. HAMMOND, JAMES N. PITTS, JR., and DONALD VALENTINE, JR. Wiley-Interscience, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1969. xiii + 588 pp. 16 × 23 cm. \$19.95.

The recent appearance of three separate surveys of the photochemical literature in addition to two review series is evidence of a

demand for a guide to the recent literature in this rapidly expanding field of research. It is reasonably clear that we do not need three separate literature surveys, and one must hope that the three groups will join forces.

The basis for consideration of the merit of a literature survey is its utility. Coverage, selection of material, ease of retrieval of information, and accuracy are obvious points to be weighed. The strong point of this survey is the stature of the authors in their

respective specialties in photochemistry. Coverage and selection of material by this outstanding group is, as one would expect, very good. The author index is set up in a very useful form that indicates which citations refer to actual references to the authors' work. The topical index is less satisfactory because of inadequate coverage. An index of compounds would be a useful addition in future volumes. The treatment of diverse fields of photochemistry, organic photochemistry, gas-phase photochemistry, and inorganic and organometallic photochemistry by scientists intimately familiar with the particular field is very desirable. The decision to separate synthetic aspects of organic photochemistry and physical organic photochemistry led to great redundancy in coverage and to an unfortunate separation of closely related information about the same reaction.

The weak points of this volume are the high cost, the long time elapsed between the literature coverage (1967) and the publication date (late 1969), and a fairly large number of errors which bother the reader. Errors such as the omission of references (cited as p 000) on p 415 and the reference to two reaction paths on p 298 when the same structure is shown after both arrows, and reference to wrong (or nonexistent) structure and equation numbers are particularly annoying. The format of the book makes reading difficult in some places because structures are separated from the appropriate text (see, for example, pp 134-140) and compounds are referred to only by number.

Chemists in all fundamental disciplines will find this volume worth browsing through. Only a few photochemists are likely to consider it for their private library.

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