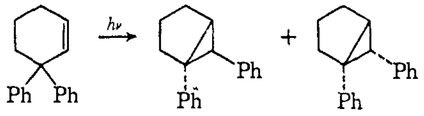
bicyclo[3.1.0]hexane. The structure **8** was proved by synthesis. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one, obtained photochemically from 4,4-diphenyl-2-cyclohexenone,[7] was converted by the standard method[6] to *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-ene, which, upon dihydrogenation, yielded **8**. It follows that **9** is the cis isomer. Thus the olefin **7** upon direct irradiation reacts in the same fashion as the conjugated analogs **1** and **4**; therefore, a conjugated diene is not a prerequisite for rearrangement.

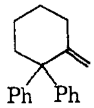


7 **8** **9**

To determine the multiplicity of the excited state involved in the transformation of **7**, the irradiation was conducted in benzene ($E_t = 85$) with a Vycor filter. Photoproducts **8** and **9** formed at about the same rate as in the direct irradiation in pentane. Also, irradiation in acetone ($E_t = 84$, Pyrex filter), which absorbed 100% of the incident light, yielded **8** and **9** at an increased rate. These results indicate that the photoreaction proceeds *via* the triplet state of **7**.

The difference in reactivity of the triplet state of **1** and **4** has been attributed to the presence of the exocyclic methylene group in **1** acting as a free rotor to dissipate energy.[3,4] In **7**, as in **4**, dissipation of the energy of the triplet cannot occur by rotation, and thus the triplets are reactive.

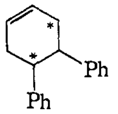
To further evaluate the role of the methylene group free rotation in photochemical reactivity, **10** was prepared from 2,2-diphenylcyclohexanone and methylenetriphenylphosphorane. Excitation of **10** under singlet or triplet conditions led to its disappearance, but no monomeric photoproducts were found.[8] In agreement with the earlier studies, the triplet of **10** is less efficient than the triplet of **7** in the vinyl–aryl di-π-methane rearrangement. It is doubtful that under the conditions employed the singlet excited state of the double bond was ever obtained. The uv spectra of **7** and **10** indicate no interaction between the phenyl and vinyl chromophores, and the absorption of an isolated double bond is minimal above 210 nm.



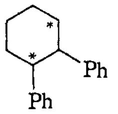
10

The photoreaction of **1** and **4** proceeded in 80% yield. The low yield of photoproduct from **7** results from two factors. First, no selection can be made between the excitation of **7** and the photoproducts **8** and **9** since all three compounds absorb light in the same region of the spectrum. Thus, when **7**, **8**, and **9** were irradiated in pentane solution with a Vycor filter under identical conditions, photoproducts **8** and **9** were consumed more rapidly than **7** by factors of 4–5.

The second factor can be illustrated by a mechanistic comparison of **7** with **1** or **4**. The greater stability of the allylic intermediate a in the reaction of **4** makes the di-π-methane reaction pathway more favorable for it than for **7** by way of intermediate b.



a



b

The photochemistry of **7** indicates that the presence of a conjugated chromophore is not a prerequisite for the vinyl–aryl di-π-methane rearrangement, although such conjugation does contribute to greater product yields. The reactivity of the triplet of **7** parallels that of the triplet of **4**. Likewise, the triplet of **10**, as the triplet of **1**, did not follow the di-π-methane pathway, a result in agreement with the proposal[3,4] that the triplets of compounds having an exocyclic methylene group dissipate the triplet energy by rotation of the exo grouping followed by efficient intersystem crossing to the ground state.

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(7) H. E. Zimmerman and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 4036 (1964).

(8) 1,1,1-Triphenyl-2-propene upon irradiation is transformed to 1,1,2-triphenylcyclopropane: G. W. Griffin, A. E. Marcantonio, H. Kristinsson, R. C. Petterson and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965).

(9) National Institutes of Health Predoctoral Fellow, 1967–1970.

(10) After this paper had been submitted for publication, Professor H. E. Zimmerman informed us he had found the same reaction.

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Electrooxidative Rearrangement of 1,1,3-Triphenylindene in Sulfur Dioxide Solvent

Sir:

Electrooxidative rearrangements are rare and largely limited to reactions which involve carbonium ion intermediates. We have been interested in ion radical rearrangements[1,2] and sought to discover a sigmatropic group migration in a cation radical. The electrooxidation of 1,1,3-triphenylindene was chosen for study since anodization should produce a cation radical which has a propensity toward 1,2-phenyl migration. The corresponding thermal,[3] photochemical,[4] and anion radical[2] rearrangements have already been disclosed. A cation radical rearrangement would, therefore, complete a set of reactions utilizing four different electronic configurations of the same atomic array. We report here on an oxidative rearrangement and on the utility of sulfur dioxide as an electrochemical solvent.

1,1,3-Triphenylindene (0.5 g, 0.009 *M*) was potentiostatically oxidized at a platinum sheet electrode using a three-compartment cell. The solvent was sulfur dioxide and the electrolyte 0.02 *M* tetrabutylammonium perchlorate. Methanol (0.033 *M*) was used as a nucleophilic trap. The temperature was held at −22° with a Dry Ice–carbon tetrachloride bath. After 8 hr at 1.2 V[5] the current had dropped from 50 to 2

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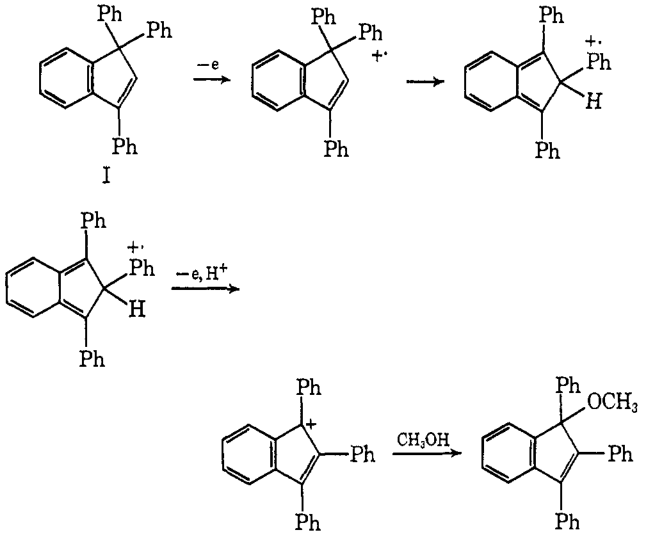
(1) L. L. Miller and L. J. Jacoby, *J. Amer. Chem. Soc.*, **91**, 1130 (1969).

(2) L. L. Miller and R. F. Boyer, *ibid.*, in press. The intermediacy of anion radicals has not been rigorously established.

(3) L. L. Miller and R. F. Boyer, *ibid.*, in press.

(4) J. J. McCullough, *Can. J. Chem.*, **46**, 43 (1968).

(5) Reference electrode Ag|0.1 *M* $AgNO_3$ in acetonitrile.



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–H_2SO_4.[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-dimethoxyindan 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 fragmentation 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^{-3} 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.

[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).

[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