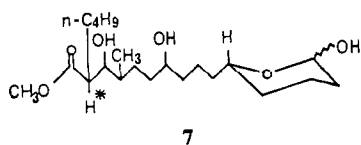
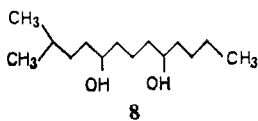


from its fragmentation pattern (partly indicated). The results also allowed the placing of the arabinose moiety. The point at which secoprimycin B was attached to C was determined by partial ozonolysis of **1** (R = Me) (at the double bond joining fragments B and C), sodium borohydride reduction, hydrolysis, and oxidation of the only free alcohol function to an acetyl group, recognized by its nmr signal.

Secoprimycin A acetate (**3**, R = Ac) was converted to the corresponding alcohol **3** (R = H), which was cleaved with sodium periodate to give the aldehyde **7**



(as hemiacetal) and acetaldehyde. Huang-Minlon reduction gave caproic acid and the diol **8** in almost



equivalent amounts and in high yields. These substances are believed to be formed by a reverse aldol-type reaction followed by reduction. The structure of **7** was shown by its fragmentation pattern. The presence of the asterisked single proton (indicating the branching) was shown by a signal at 2.7 ppm in the nmr spectrum. In addition, treatment of **3** (R = Ac) with mild base gave the corresponding  $\alpha,\beta$ -unsaturated ester, albeit in small yield. These data together with the fact that secoprimycin A has three C-methyl groups establishes its structure.<sup>9</sup> The point of attachment of secoprimycin A to secoprimycin B was shown by a borodeuteride experiment. The deuterium was introduced at the position marked with a dagger in **3**.

Methylation of secoprimycin B (**4**, R = H) gave the ether **4** (R = Me), which, on mild acid hydrolysis in methanol, gave the arabinose as the methyl-2,3,5-tri-*O*-methyl-D-arabofuranoside, identified by its mass spectrum.<sup>10</sup> That the sugar is attached as the  $\alpha$  anomer is suggested by the presence of the acetal methine hydrogen as a singlet<sup>11</sup> at ca. 5.2 ppm in the spectrum of derivatives of secoprimycin B.

The above evidence requires that primycin be represented as **1** (R = H).

**Acknowledgment.** We wish to thank the Antibiotic Service of the Pharmaceutical Research Institute for

(9) Secoprimycin A was not obtained in pure homogeneous form but contained small amounts of congeners.

(10) K. Heyns and H. Scharmann, *Tetrahedron*, **21**, 507 (1965).

(11) J. D. Stevens and H. G. Fletcher, Jr., *J. Org. Chem.*, **33**, 1799 (1968); L. D. Hall and P. R. Steiner, *Can. J. Chem.*, **48**, 1155 (1970); K. L. Rinehart, W. S. Chilton, M. Hichens, and W. V. Phillipsborn, *J. Amer. Chem. Soc.*, **84**, 3216 (1962).

the fermentation, at Budapest, of a new strain producing primycin (*Thermopolyspora galeriensis*).

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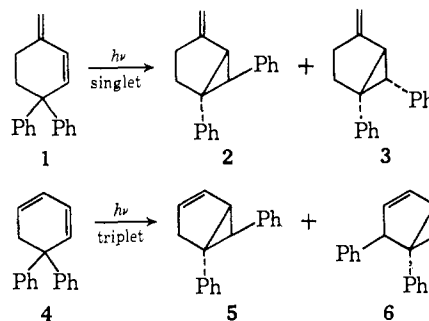
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### Photochemistry of 3,3-Diphenylcyclohexene. The Vinyl-Aryl Di- $\pi$ -methane Rearrangement in a Nonconjugated System<sup>1</sup>

Sir:

Recently, much interest has been directed toward the study of the photochemical vinyl-aryl di- $\pi$ -methane rearrangement in conjugated diene systems. For example, **1**, upon direct irradiation, gives **2** and **3** via a singlet path, whereas the triplet of **1** is unreactive.<sup>2</sup> On the other hand, the endocyclic isomer **4** gives **5** and **6** only under triplet-sensitized conditions.<sup>3,4</sup> The present study has investigated the photochemistry of **7**, the nonconjugated analog of this series, in order to determine the role conjugation plays in the rearrangement.



The olefin **7** (mp 31–32°) was synthesized in 90% yield from 2,2-diphenylcyclohexanone<sup>5</sup> via the *p*-toluenesulfonylhydrazone-methyl lithium process.<sup>6</sup> When **7** was irradiated in pentane (Vycor filter), the yield of two major photoproducts was maximized when 21% of the starting material had reacted. The remaining starting material was removed by oxidative ozonolysis and the two photoproducts **8** and **9** were isolated by silica gel chromatography, each in 6% yield; **8** was a liquid and **9** was a solid (mp 66–68°). The nmr and mass spectra of these two compounds indicated that they were *cis* and *trans* isomers of 5,6-diphenyl-

(1) This work was supported, in part, by Grant No. AM-00709, from the National Institute of Arthritis and Metabolic Diseases of the U. S. Public Health Service.

(2) H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **89**, 5971 (1967); **91**, 5307 (1969).

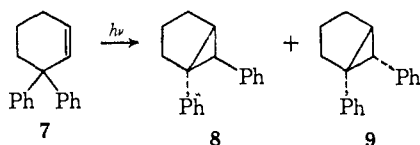
(3) J. S. Swenton, A. R. Crumxine, and T. J. Walker, *ibid.*, **92**, 1406 (1970).

(4) H. E. Zimmerman and G. A. Epling, *ibid.*, **92**, 1411 (1970).

(5) H. E. Zaugg, M. Freifelder, and B. W. Horrom, *J. Org. Chem.*, **15**, 1191 (1950).

(6) W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Amer. Chem. Soc.*, **90**, 4762 (1968).

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,<sup>7</sup> was converted by the standard method<sup>6</sup> 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 ir-

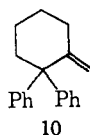


radiation reacts in the same fashion as the conjugated analogs **1** and **4**; therefore, a conjugated diene is not a prerequisite for rearrangement.

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.<sup>3,4</sup> 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.<sup>8</sup> In agreement with the earlier studies, the triplet of **10** is less



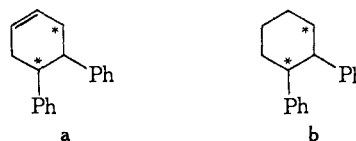
efficient than the triplet of **7** in the vinyl-aryl di- $\pi$ -methane rearrangement. It is doubtful that under the conditions employed the singlet excited state of the double bond was ever obtained. The uv spectra of **7** and **10** indicate no interaction between the phenyl and vinyl chromophores, and the absorption of an isolated double bond is minimal above 210 nm.

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.

(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).

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- $\pi$ -methane reaction pathway more favorable for it than for **7** by way of intermediate **b**.



The photochemistry of **7** indicates that the presence of a conjugated chromophore is not a prerequisite for the vinyl-aryl di- $\pi$ -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- $\pi$ -methane pathway, a result in agreement with the proposal<sup>3,4</sup> 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.

(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<sup>1,2</sup> 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,<sup>3</sup> photochemical,<sup>4</sup> and anion radical<sup>2</sup> 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  $-22^\circ$  with a Dry Ice-carbon tetrachloride bath. After 8 hr at 1.2 V<sup>5</sup> the current had dropped from 50 to 2

(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<sub>3</sub> in acetonitrile.