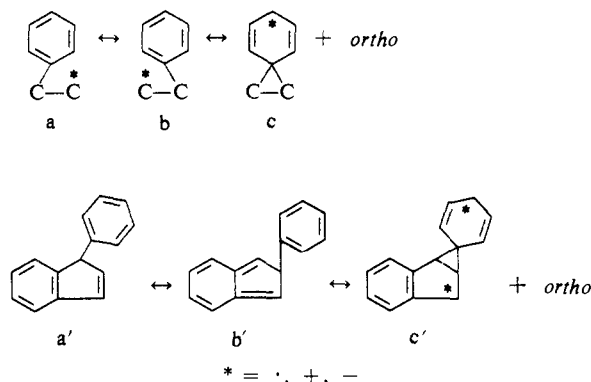


supported by the observation that phenyl, which has low-lying π orbitals of inverted symmetry,⁴ migrates with efficiency intermediate between hydrogen and methyl. These aptitudes are in direct contrast to those found in 1,2-anionic,¹³ free-radical,¹⁴ and cationic¹⁵ rearrangements where phenyl always migrates as well as or to the exclusion of hydrogen and methyl. This incongruity can be rationalized by considering the transition-state structures shown in Scheme I. Structure

Scheme I



c can account for the preference for phenyl migration in anion, cation, and radical rearrangements. In thermal, neutral molecule rearrangements, however, structure c' should be considerably less important since it is diradical or dipolar and a' and b' are not. This indicates that in the absence of a necessity to delocalize charge or an odd electron, hydrogen may ordinarily be a better migrating group, *i.e.*, a bridged hydrogen is more stable relative to its unbridged precursor than is a bridged carbon relative to its precursor. Although energy matching is washed out by the comparison of reactants and transition states, the overlap capabilities of the unidirectional hydrogen orbital compared with carbon orbitals is a credible explanation for this difference. We hope to test these speculations by making a more extensive study of migratory aptitudes in the indene series and in other thermal, neutral molecule sigmatropic rearrangements.

(13) H. E. Zimmerman in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 391.

(14) C. Walling in ref 13, p 409.

(15) See S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952), and references cited there.

(16) Participant in National Science Foundation Research Participation for High School Teachers Program, Colorado State University.

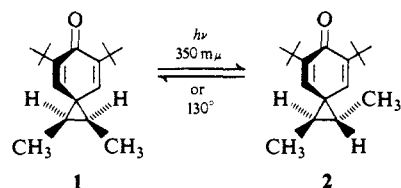
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Received December 23, 1968

Stereospecificity and Wavelength Dependence in the Photochemical Rearrangement of Spiro[2.5]octa-4,7-dien-6-ones to Quinone Methides

Sir:

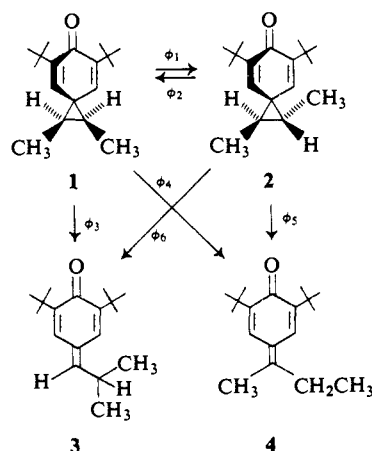
The photochemistry of spirodienones **1** and **2** is of unusual interest. Not only do these compounds undergo stereospecific photochemical rearrangements, but the type of reaction observed is dependent upon the wavelength of the incident light.

Spirodienones **1** and **2** are thermally and photochemically interconvertible. *n*-Decane solutions of the *cis* isomer **1** isomerize to the *trans* isomer **2** with a half-life of *ca.* 1 hr at 150° and afford a 1.8 ± 0.2:1.0 equilibrium mixture with the *trans* isomer predominating. Prolonged heating at 240° affords no other detectable¹ products and does not appreciably alter the equilibrium position. Irradiation² of *only* the long-wavelength absorption bands of **1** or **2** (λ_{\max} 352 m μ (ϵ 38 or 39, respectively)) affords, in cyclohexane, a 4:1 photostationary mixture favoring *trans*-**2** and leads to no other products, or to material loss.¹ The absorption spectra of **1** and **2** are sufficiently similar so that no appreciable optical pumping can occur in the ultraviolet region. Photosensitized *cis*-*trans* isomerization also occurs with results comparable³ to those of the 350-m μ direct irradiation.



In contrast, 254-m μ irradiation⁴ of **1** or **2** (degassed 0.4 *M* cyclohexane solutions in quartz nmr tubes) leads not only to *cis*-*trans* isomerization but also affords quinone methides **3** and **4** *via* methyl or hydrogen migration.⁵ Figures 1 and 2 illustrate the relative concentrations of **1**, **2**, **3**, and **4** as a function of time. Since no other products are detectable,¹ total concentrations are assumed to remain constant. From Figures 1 and 2, it is qualitatively apparent that, in competition with the faster *cis*-*trans* isomerization, *cis*-**1** affords preferential methyl migration while *trans*-**2** affords preferential hydrogen migration. Using the experimentally deter-

Scheme I



(1) Analyses were performed *via* 100-MHz nmr spectroscopy.

(2) Irradiations were conducted using Pyrex vessels in a Rayonet photochemical reactor equipped with 3500-Å lamps. Solutions were degassed and maintained at *ca.* 5° during irradiation. Dienone concentrations were such that >99% of the incident light was absorbed.

(3) During the 350-m μ irradiation of **1**, the presence of sufficient acetophenone-*d*₈ (deuteriated to simplify nmr analysis) to absorb *ca.* 40% of the incident light fails to affect either the rate of attainment or the position of the photoequilibrium relative to that of an unsensitized but otherwise identical control.

(4) Irradiations were conducted at *ca.* 5° in a Rayonet photochemical reactor equipped with 2537-Å lamps. At least 99% of the incident light was absorbed.

(5) W. H. Pirkle and G. F. Koser, *Tetrahedron Lett.*, 129 (1968).

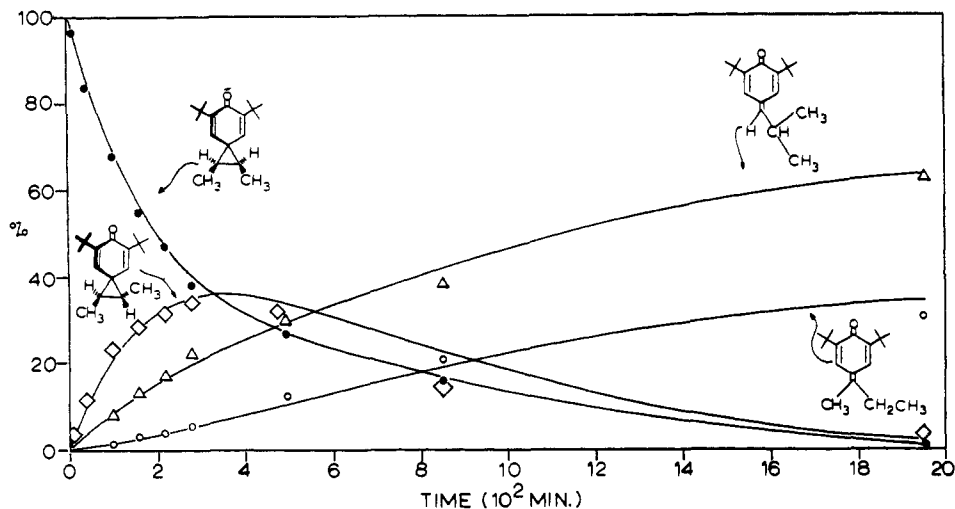


Figure 1. The relative ratios of **1**, **2**, **3**, and **4** as a function of time upon photolysis of **1** at 3537 Å. Computer-generated curves and experimental points are shown.

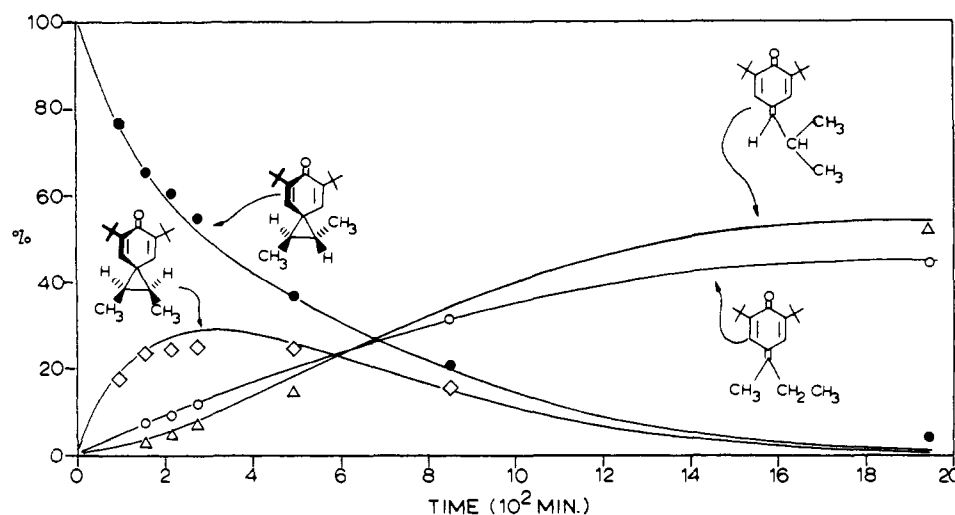


Figure 2. The relative ratios of **1**, **2**, **3**, and **4** as a function of time upon photolysis of **2** at 2537 Å. Computer-generated curves and experimental points are shown.

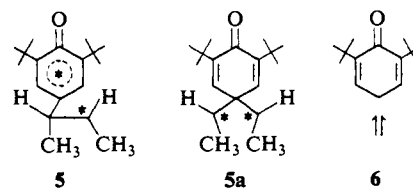
mined 254-m μ molar extinction coefficients (*i.e.*, 5660, 5800, 1090, and 800, respectively) of **1**, **2**, **3**, and **4**, relative quantum yields which afford close correspondence to the kinetic data were obtained by simulating Scheme I on an EIA TR 20 analog computer. Relative values for ϕ_1, \dots, ϕ_6 of 25, 19.6, 9.0, 0.90, 3.73, and 0.0 were used to generate the curves shown in Figures 1 and 2. From the empirically obtained relative quantum yields it appears that *cis*-**1** affords essentially only methyl migration, whereas *trans*-**2** affords essentially only hydrogen migration.

Because the 254-m μ photoinduced rearrangements of **1** and **2** are quite stereospecific, it is manifest that these migration reactions involve distinctly different intermediates than do any of the *cis*-*trans* isomerizations.⁶ In

(6) For instance, should a cyclopropane ring opened intermediate such as **5** obtain, the migrations would have to be at least ten times as fast as rotation about the σ bond to account for the observed stereospecificities, since such rotation would cause loss of the stereochemical distinction between the ring-opened intermediates from *cis*-**1** and from

addition, it appears that different intermediates are involved in some of the *cis*-*trans* isomerizations.⁷

Both the photochemical and the thermal *cis*-*trans*



trans-**2**. However, under all of the previously mentioned reaction conditions, the *cis*-*trans* isomerization (*i.e.*, rotation and closure) is faster than migration (see Figures 1 and 2). Hence, common intermediates cannot be involved in these reactions.

(7) For example, the composition of the thermally equilibrated mixture (*i.e.*, *trans*:*cis* ratio 1.8 ± 0.2) is similar to that of the 254-m μ photostationary state (*i.e.*, ϕ_1/ϕ_2 1.3 ± 0.3), as might be expected if similar intermediates are involved. However, the rather different composition (*i.e.*, *trans*:*cis* ratio 4 ± 0.5) of the photostationary mixture obtained upon sensitized³ or unsensitized irradiation at 350 m μ suggests that intermediates differing in multiplicity and/or structure must be involved in these isomerizations.

isomerizations of **1** and **2** must involve cyclopropane ring opened species. Since the thermal reaction undoubtedly occurs with conservation of spin, the thermally opened singlet intermediate⁸ is likely to be **5** rather than **5a**, which presumably would be of considerably higher energy. It is significant that no quinone methides are produced thermally, which suggests that ground-state singlet 1,3 diradicals such as **5** may close but do not rearrange.⁹ From the observation that neither quinone methide **3** nor **4** are formed during the addition of triplet carbene **6** to *cis*-2-butene,¹⁰ it is obvious that triplet **5** also closes but does not rearrange. Since neither 350-m μ light-induced nor photosensitized³ *cis*-*trans* isomerization of **1** or **2** affords quinone methides, triplet **5** could be an intermediate in either or both of these reactions. However, the possibility that the species thus obtained is **5a** rather than **5** cannot be presently excluded. While species **5a** could suffice for *cis*-*trans* isomerization, it is not a likely precursor of methyl or hydrogen migration.

Acknowledgment. This work has been supported by an unrestricted research grant from the Rohm and Haas Company.

(8) Whether this intermediate should be considered as diradical or as dipolar is debatable, although the former certainly seems preferable in terms of energetics and observed chemistry.

(9) There are numerous instances in the literature where singlet 1,3 diradicals, generated either thermally or photochemically, have been thought to rearrange to afford propenes. For example, see D. I. Schuster and I. Krull, *J. Mol. Photochem.*, in press; E. T. McBee, J. A. Bosoms, and C. J. Morton, *J. Org. Chem.*, **31**, 768 (1966); R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **88**, 3963 (1966), and references therein.

(10) W. H. Pirkle and G. F. Koser, *Tetrahedron Lett.*, 5959 (1968).

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Received November 30, 1968

Oligonucleotide Studies. VII. Optical Rotatory Dispersion of Adenylyl-(3'-5')-4-thiouridine and Guanylyl-(3'-5')-4-thiouridine¹

Sir:

Some new findings on the optical properties of the two 4-thiouridine-containing dinucleoside monophosphates, adenylyl-(3'-5')-4-thiouridine (ApTU) and guanylyl-(3'-5')-4-thiouridine (GpTU), are presented. These results are believed to be useful for the sequence analysis of 4-thiouridine-containing oligonucleotides obtainable from the pancreatic ribonuclease (RNase IA; EC 2.7.7.16) treatment of *E. coli* transfer ribonucleic acids (tRNA) as well as for understanding the conformation of such oligonucleotide segments in those tRNA molecules.

A study of these two particular dinucleoside monophosphates of eight possible 4-thiouridine-containing dimers made up of 4-thiouridine and the four major nucleotides is now warranted by the recurrence of a - - - - PuTU - - - - and/or - - - - PuPuTU - - - - sequence in *E. coli* tRNA as recently found by Lipsett.² Furthermore, the current problem of determining the nucleotide sequence of some 4-thiouridine-containing species of

(1) Part VI in this series is by S. Aoyagi and Y. Inoue, *J. Biochem. (Tokyo)*, **64**, 603 (1968).

(2) M. N. Lipsett, Abstracts, Symposium on Transfer of Genetic Information in Protein Synthesis, New York, N. Y., June 7-8, 1968.

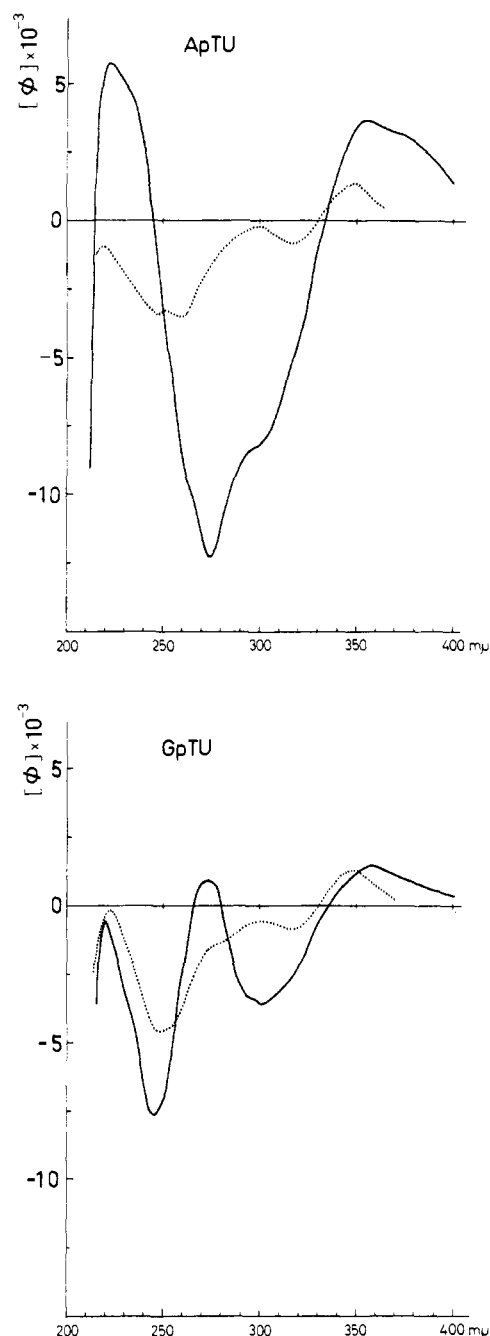


Figure 1. The ORD spectra of ApTU and GpTU at pH 5.8, 25°, and ionic strength 0.1 (—), and of their corresponding components, 5'-AMP + TU and 5'-GMP + TU (.....). $[\phi]$ is molecular rotation per residue, defined as $[\phi] = [M]/2$.

tRNA, which is being actively pursued in many laboratories, prompts us to report our results on the ultraviolet absorption and optical rotatory dispersion of ApTU and GpTU.

ApTU and GpTU were respectively prepared with the aid of a synthetic reaction³ by RNase U₂ from *Ustilago sphaerogena* and RNase N₁ from *Neurospora crassa*, both of which were discovered in our laboratories.^{4,5}

(3) F. Egami, T. Uchida, T. Arima, and T. Koike, Fifth International Symposium on the Chemistry of Natural Products, London, 1968, Abstracts, E-20, 266.

(4) T. Arima, T. Uchida, and F. Egami, *Biochem. J.*, **106**, 609 (1968).

(5) N. Takai, T. Uchida, and F. Egami, *Biochim. Biophys. Acta*, **128**, 218 (1966).