

arenedienes. This may correspond to the 1L_b band of benzene;¹³ if so, it is apparently slightly red shifted. The intense maxima which occur variously from 2310 to 2450 Å are probably related to the first π, π^* transition of butadiene,¹⁴ with a large red shift and an increase in oscillator strength. Since both features fall at long wavelength relative to the transitions in the reference compounds, more than two excited states must be interacting. If the intense maximum is related to the butadiene transition, it must be mixed with other benzene-like transitions in addition to the 1L_b band. This is in no way surprising but indicates that definitive analysis of the spectra will require data from the vacuum ultraviolet. Key features of the spectra of three of the compounds are shown in Figure 1.

Even though chromophoric groups are directly coupled, the cooperative chemical reaction is not rapid enough to become the dominant mode of decay. We have not determined quantum yields for the cyclization, but they must be rather low, since *cis-trans* isomerization is more rapid. The mechanism of isomerization is in itself interesting and may be related to either or both of two other phenomena: (1) quenching of excited singlet states of aromatic hydrocarbons by conjugated dienes¹⁶ and (2) the fact that all attempts to effect ring closure of compounds **1** using photosensitizers as the primary light absorbers have been totally unsuccessful. Energy is, however, transferred to the substrates because *cis-trans* isomerization occurs. Apparently, as was the case with the phenylpropenes,^{6,7} ring closure occurs only in the excited singlet states, not in the triplets formed by energy transfer.

Acknowledgment. This work was supported by the Directorate of Chemical Services, Air Force Office of Scientific Research, under Contract No. AF 49(638)-1479.

(13) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

(14) According to Woodward's rules¹⁵ the 2100-Å maximum of butadiene is shifted 50 Å to the red for each alkyl substituent on the diene unit. Thus the predicted maxima for the compounds whose spectra are shown in Figure 1 are: **1a**, 2250 Å, and **1c**, 2200 Å.

(15) R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 72 (1942).

(16) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, **88**, 3665 (1966).

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Mechanisms of Photochemical Reactions in Solution. XLVIII.¹ Rearrangement of Phenylvinylcyclopropanes

Sir:

In the accompanying communication we have described the preparation of *cis*- and *trans*-3,3-dimethyl-2-(2',2'-dimethylvinyl)-1-phenylcyclopropane (**2a** and **2b**, respectively, 90% yield). The compounds are themselves photolabile when irradiated with a mercury resonance lamp. This reactivity is not a complication in the preparation of **2a** and **2b** since the acyclic pre-

(1) Part XLVII: H. Kristinsson and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 5968 (1967).

cursors (compounds **1** in ref 1) absorb more strongly² than the cyclopropane derivatives.

As is shown in Chart I, irradiation of **2a** and **2b** gives the same set of products which include neither the dienes from which the cyclopropanes were prepared nor the cyclopentene that would have been expected from thermal rearrangement of a vinylcyclopropane.³ The photoproducts **3**, **4**, and **5** are produced in the ratio 1:6:2. The principal product formed by path B was isolated in 50% yield by vapor chromatography and shown to consist of two constituents, **4a** and **4b**, in the ratio 1:2.2. The structure of **5** was assigned on spectral evidence.⁴ Infrared and nmr spectra of both **5** and the compound to which it was converted on hydrogenation showed that the substances contained disubstituted benzene nuclei. All nmr resonances of both compounds were compatible with the structure shown.

The assignment of structures to **4a** and **4b** is based on both chemical and spectral evidence. The nmr spectra show the absence of vinyl protons, the presence of four methyl groups, signals at relatively high field due to the bridgehead protons, and signals at lower field for the benzylic protons. The *syn* structure is assigned to **4a** because the resonance from the benzylic proton is split into a doublet, with $J = 2$ cps, centered at τ 7.10. The corresponding signal in **4b** occurs as a singlet at τ 7.12. Vicinal protons attached to cyclobutanes have generally been found to be more strongly coupled in the *cis* than in the *trans* configuration. A confirmatory indication is provided by the occurrence of the signal due to bridgehead protons in **4b** at relatively high field (τ 9.02 and 8.91) compared to **4a** (τ 8.43 and 8.34), probably because of the diamagnetic anisotropy of the adjacent phenyl group. The ultraviolet spectra of both compounds resemble those of alkylbenzenes.

Assignment of the more strained *syn* structure to **4a** is consistent with its chemical reactivity. On being heated to 250° the compound undergoes smooth conversion to a single product. The isomer **4b** is stable at 250° but at 290° is converted to four products, none of which has vapor chromatographic retention times equal to the product from **4a**. One of the products from **4b** does have the same retention time as **7**, a compound formed more conveniently by acid-catalyzed rearrangement of the bicyclopentanes. No attempt has been made to isolate and characterize the pyrolysis products. No interconversion of **4a** and **4b** was observed in the pyrolytic experiments.

Compound **4a** is hydrogenated smoothly to **9** at atmospheric pressure and room temperature in the presence of palladium on charcoal; **4b**, on the other hand, resisted most attempted hydrogenations in the presence of the same catalyst as well as metallic platinum and Raney nickel. In a single experiment hydrogen was taken up and **6**, identical with material produced by hydrogenation of **7**, was formed. We believe that rearrangement to **7**, catalyzed by adventitious acid, preceded hydrogenation.

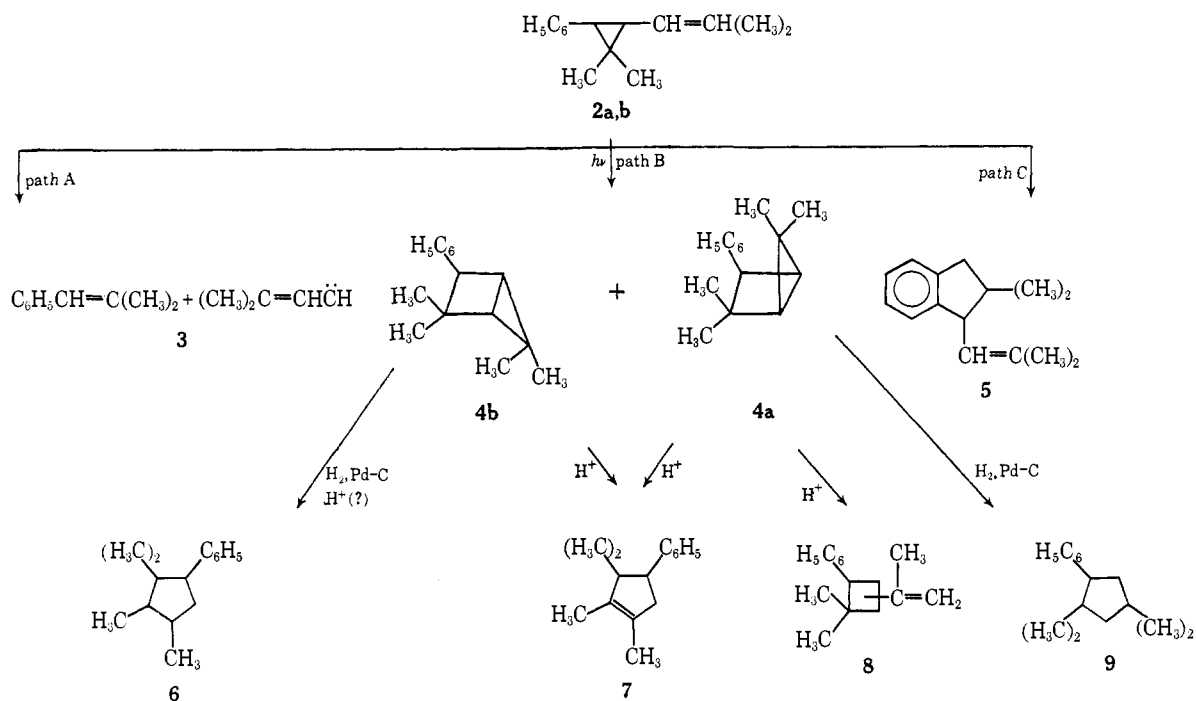
Acid-catalyzed isomerization of the bicyclopentanes is almost completely stereospecific. On treatment with

(2) The values of ϵ_{\max} at 2537 Å are about 16,200 for the acyclic compounds and about 1000 for the cyclopropane.

(3) C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 4896 (1960).

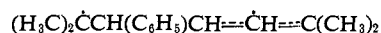
(4) Satisfactory elementary analyses were obtained for all new compounds.

Chart I



hydrochloric acid in ether at room temperature, **4b** rearranges exclusively with methyl migration to give **7** as the major product, whereas **4a** gives **8** and a trace of **7**. The point of attachment of the isopropenyl group to the four-membered ring in **8** has not been determined. Rearrangement of bicyclopentanes with breaking of one of the bonds external to the four-membered ring is unprecedented.⁵ A concerted mechanism for proton-assisted rearrangement of **4b** to **7** is easily formulated, but it is not clear that the same kind of mechanism should not be equally available for conversion of **4a** to **7**. In short, we do not have a useful rationalization of the stereospecificity of the acid-catalyzed reactions.

Specificity in the photorearrangements of **2** is also interesting. There is no overlap of products obtained from **1** and **2** in agreement with the hypothesis that the original formation of **2** involves diradical **10**, and the isomerization of **2** involves **11**. Surprisingly, neither

**10****11**

reaction leads to formation of cyclopentenes. The only logical basis that we can see for exclusion of this expected product is the presumption that the allylic units of **10** and **11** are formed with exclusively *trans* stereochemistry.

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(5) R. T. LaLonde and L. S. Forney, *J. Am. Chem. Soc.*, **85**, 3767 (1963).

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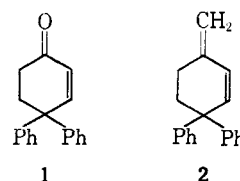
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Methylene Analogs of Cyclohexenones. Mechanistic and Exploratory Organic Photochemistry. XXVIII¹

Sir:

We have undertaken an investigation of the photochemistry of methylene analogs of ketones in order to determine the behavior of compounds lacking $n-\pi^*$ excited states. Accordingly, the methylene analog **2** of 4,4-diphenylcyclohexenone (**1**) was selected, since this enone has been investigated in some detail.²

**1****2**

1-Methylene-4,4-diphenylcyclohex-2-ene (**2**) was prepared from the Wittig reaction of methylenetriphenylphosphorane with **1**. Silica gel chromatography and distillation gave **2** as a colorless oil:³ bp 125–127° (0.05 mm); $\lambda_{max}^{E:OH}$ 232 m μ (ϵ 31,000), 238 (31,600), 263 sh (1740), and 270 sh (1160); infrared (neat) 6.11 and

(1) Paper XXVII: H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. Zimmerman, *J. Am. Chem. Soc.*, in press.

(2) (a) H. E. Zimmerman and J. W. Wilson, *ibid.*, **86**, 4036 (1964); (b) H. E. Zimmerman and K. G. Hancock, Abstracts, 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967, O-130, 1967, O-130.

(3) All compounds described gave acceptable analyses.