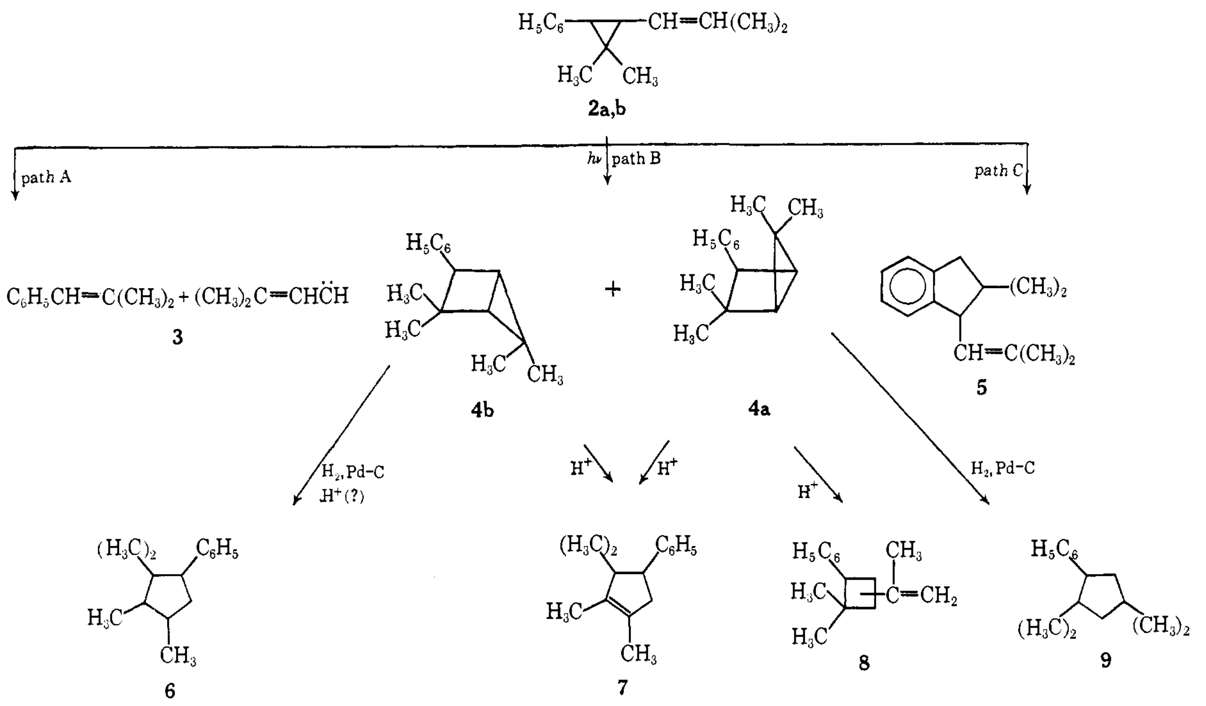
**Chart I**



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

$(H_3C)_2\dot{C}CH(C_6H_5)CH{=}\dot{C}H{=}C(CH_3)_2$

**10**

$C_6H_5\dot{C}HC(CH_3)_2CH{=}\dot{C}H{=}C(CH_3)_2$

**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.

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

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*Received May 5, 1967*

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

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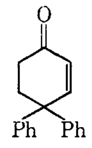
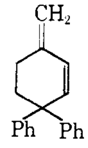
## Methylene Analogs of Cyclohexenones. Mechanistic and Exploratory Organic Photochemistry. XXVIII[1]

*Sir:*

We have undertaken an investigation of the photochemistry of methylene analogs of ketones in order to determine the behavior of compounds lacking n–π* 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); $\lambda_{\max}^{\mathrm{EtOH}}$ 232 mμ (ε 31,000), 238 (31,600), 263 sh (1740), and 270 sh (1160); infrared (neat) 6.11 and

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(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, 1967, O-130.

(3) All compounds described gave acceptable analyses.

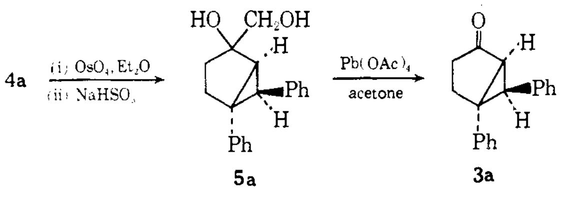
11.30 μ; nmr ($CCl_4$) τ 2.80 singlet (10 H, aromatic), AB quartet centered at 3.79 ($\delta_A$–$\delta_B$ = 0.19 ppm, 2 H, –CH=CH–, $J_{AB}$ = 10 cps), 5.18 br singlet (2 H, =$CH_2$), and 7.70 singlet (4 H, ring $CH_2$).

Since **1** is known[2] to rearrange *via* a triplet with phenyl migration to give *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**3a, b**), we initially sought to generate the triplet of **2** by benzophenone ($E_T$ = 68.8 kcal/mole) sensitization under conditions where benzophenone absorbed over 97.5% of the light. In contrast to the enone case, no phenyl migration products could be detected, and monomeric products were not obtained. That triplet transfer was effective was shown by quenching by **2** of benzopinacol formation with added benzhydrol.

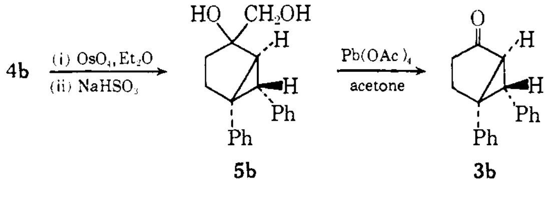
On the other hand, direct irradiation (λ >220 mμ, Vycor filter) gave two isomeric products which could be partially separated by deactivated silicic acid chromatography. Nmr analysis of the reaction *vs.* time revealed no other primary products. Typically, 2 hr was required for 80% conversion.

The major product was identified as *trans*-5,6-diphenyl-2-methylenebicyclo[3.1.0]hexane (**4a**), while the minor product (*ca.* 10% by nmr) was shown to be *cis*-5,6-diphenyl-2-methylenebicyclo[3.1.0]hexane (**4b**). The structure proofs rested on degradation to the known bicyclic ketones **3a** and **3b** and on independent synthesis of each. Spectral data for **4a** were: nmr ($CCl_4$) τ 2.70 singlet (10 H, aromatic), broad 4.90 and 5.20 singlets (2 H, =$CH_2$), 7.42 singlet (2 H, ring $CH_2$), 7.7–8.3 multiplet (4 H, ring $CH_2$ and cyclopropyl CH-CH); infrared ($CS_2$) 6.06, 11.50, and 11.59 μ. Spectral data for **4b** were: nmr ($CCl_4$) τ 2.80–3.40 multiplet (10 H, aromatic), 4.95 and 5.17 slightly split singlets (2 H, =$CH_2$, $J$ = 1.5 cps), 7.30–8.05 multiplet (6 H, ring $CH_2$ and CH); infrared ($CS_2$) 6.05 and 11.49 μ. The nmr and infrared spectra were superimposable on those of synthetic **4a** and **4b** prepared by the Wittig reaction of methylenetriphenylphosphorane with *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**3a** and **3b**), respectively.

The degradation involved oxidation to the corresponding ketones **3a** and **3b** by means of osmium tetroxide followed by lead tetraacetate in acetone (eq 1 and 2).



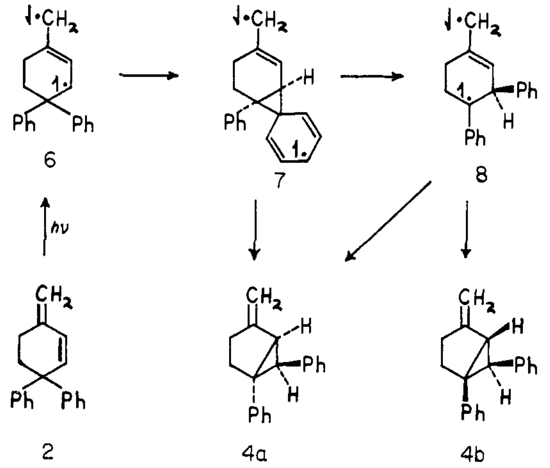
(1)



(2)

Thus the over-all reaction can be pictured as shown in Scheme I. Here excitation affords the π–π* excited singlet **6** which is depicted as undergoing bridging to afford **7**. The preferred formation of stereoisomer **4a** can be understood if **7** collapses directly to product with loss of electronic excitation and with inversion of configuration at C-4. Alternatively, completion of migration affords **8** which can lead to either stereoisomer **4a** or **4b**. An analogous rationale was employed to explain the similar stereochemistry found in the 4,4-diphenylcyclohexenone rearrangement.[4]

**Scheme I**



It is interesting to note that despite the remarkable structural similarities of the ketone and hydrocarbon reaction,[5] there remain striking differences. Intersystem crossing to the triplet in the case of diene **2** must be much slower than the rate of phenyl migration in the singlet excited state **6**. This doubtlessly derives from spin–orbit coupling enhancing the rate of intersystem crossing in the ketone case. Most remarkable is the reluctance of the hydrocarbon triplet to rearrange, since in the enone (**1**) photolysis the triplet is quite willing to do so. However, we do note that in the ketone rearrangement there is an n–π* excited state not available in the present system.

We are pursuing quantitative aspects of this research as well as the effect of electronegativity of the exocyclic moiety.

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(4) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 2033 (1967).

(5) One might concern himself about localization of excitation presently in a different moiety than in the enone case. However, as noted in our earlier publications (*e.g.*, ref 4), as phenyl migration begins, overlap results in an elongated π system and consequent spreading out of the electronic excitation. In the present case of **2**, it is uncertain[6] whether excitation is initially heavily localized[7] in the phenyl or the diene group prior to migration. But migration leads to an extended chromophore now including the original diene and phenyl moieties; hence, independent of which group absorbs, the same route is likely to be followed.

(6) In the case of the triplet the lower energy grouping is the diene ($E_T$ = –59 kcal/mole *vs.* –80 kcal/mole for phenyl), and no uncertainty exists. The hydrocarbon triplet, even prior to change, provides a valid model for a π–π* excited enone triplet. For the singlet the 0–0 energies of the phenyl and diene groups may be close. Thus Srinivasan[8] has estimated a 107-kcal/mole (~266 mμ) 0–0 band for butadiene; the present moiety will be lower in energy. The 0–0 band of alkyl-substituted benzenes is at 266 mμ (107 kcal/mole).[9]

(7) The ultraviolet absorption spectrum of the reactant has a maximum (*vide supra*) which is reasonably close to that of purely aliphatic analogs [*e.g.*, 237 mμ (20,000) for 7-methylenecholesterol[10] and 231 mμ (9200) for β-phellandrene[11]]. Thus there is no convincing evidence for pronounced initial state conjugation.

(8) R. Srinivasan, *Advan. Photochem.*, **4**, 117 (1966).

(9) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 254.

(10) B. Bann, I. M. Heilbron, and F. S. Spring, *J. Chem. Soc.*, 1274 (1936).

(11) H. Booker, L. K. Evans, and A. E. Gillan, *ibid.*, 1453 (1940).

**Acknowledgment.** Appreciation is expressed for WARF and NSF predoctoral fellowships awarded to G. E. S.

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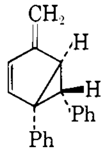
## $\pi-\pi^*$ Rearrangements. The Photochemistry of 1-Methylene-4,4-diphenyl-2,5-cyclohexadiene as a Dienone Analog. Mechanistic and Exploratory Organic Photochemistry. XXIX[1]

*Sir:*

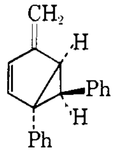
The 4,4-diphenylcyclohexadienone (**1**) system has been studied extensively and a mechanistic rationale proposed for the type-A[2] rearrangement observed.[3] This mechanism involved $\beta,\beta$ bonding of the $n-\pi^*$ excited triplet.[3c] It therefore seemed of considerable import to inspect the photochemistry of a system lacking $n-\pi^*$ excitation but having the same $\pi$ system. To this end 1-methylene-4,4-diphenyl-2,5-cyclohexadiene (**2**) was studied. This was prepared by the reaction of 4,4-diphenylcyclohexadienone (**1**) with methylenetriphenylphosphorane.

Irradiation of 1-methylene-4,4-diphenyl-2,5-cyclohexadiene (**2**) in *t*-butyl alcohol with a Vycor filter afforded two main products. The first, mp 58.5–59.0°, appeared to be the major initial product and was accompanied by an oil which appeared to derive from the 59° product and which accumulated with time.

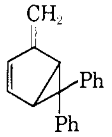
Analytical data[4] on the 59° primary photoproduct showed it to be isomeric with reactant **2**. The infrared and nmr suggested a methylenebicyclo[3.1.0]hex-2-ene (11.38 $\mu$ and $\tau$ 4.83, 4.98). Thus structures **3** and **4** were strong possibilities. A type-A rearrangement analogous to that of dienones would give **4**, while phenyl migration similar to that of 4,4-diphenylcyclohexenone[5] would afford **3**. Osmium tetroxide oxidation of the 59° photoproduct gave two glycols, mp 136–137 and 117–118°. Lead tetraacetate oxidation of the latter (**5**) gave an unsaturated bicyclic ketone **6** whose structure[6] and stereochemistry were determined by hydrogenation over $PtO_2$ (EtOAc–$Et_3N$) to the known[5] *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**7**).



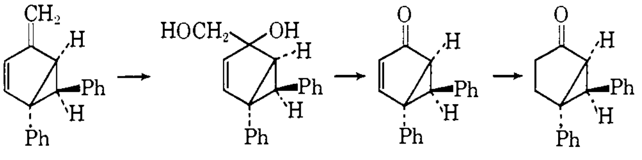
**3a**



**3b**



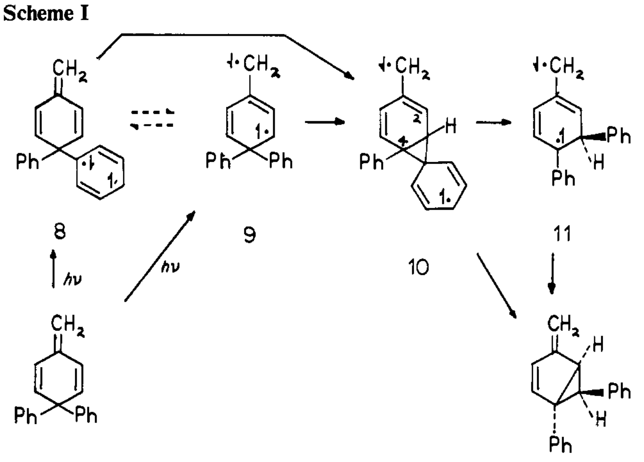
**4**



**3b** **5** **6** **7**

We can conclude that the 59° photoproduct has structure **3b**, and thus the rearrangement did not follow the type-A route taken so facilely[3c,d] by the dienone **1**. However, the dienone reacts *via* the triplet,[3c,d] and thus the reaction of **2** with sufficient benzophenone present to absorb 99% of the light (Pyrex filter) was studied. None of the ordinary photoproduct **3b** was found, and the reactant was remarkably stable to these sensitization conditions. To ascertain that triplet transfer was actually effected, the benzophenone experiment was rerun with benzhydrol present and with **2** present in one run and absent in another.[7] A 97% decrease in benzopinacol formation when **2** was present demonstrated transfer of triplet excitation to **2**. The reaction may be depicted as shown in Scheme I.

**Scheme I**



**8** **9** **10** **11** **2** **3b**

In assessing the reasons for the differing behavior of the present methylene analog from that of the dienone **1**, we recognize that slower intersystem crossing due to lack of spin–orbit coupling tends to favor reactions of the singlet and that in the present case phenyl migration manages to compete favorably with intersystem crossing. It is interesting, however, that the singlet reaction is quite similar to the rearrangement of the $n-\pi^*$ triplet of enones.[5] Additionally, it is remarkable that the singlet excited state rearranges but the triplet does not. One possibility is that this difference derives from the triplet excitation being heavily localized in the cross-conjugated triene moiety ($E_T \leq 60$ kcal/mole) rather than the phenyl group ($E_T = 80$ kcal/mole), while in the excited singlet the two moieties[8] have similar energies. It is possible that availability of phenyl excitation facilitates migration in such $\pi-\pi^*$ systems.

Another point of interest is the highly stereoselective reaction course. This is understood if the completion

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(1) Paper XXVIII: H. E. Zimmerman and G. E. Samuelson, *J. Am. Chem. Soc.*, **89**, 5971 (1967).

(2) H. E. Zimmerman, *Science*, **153**, 837 (1966).

(3) (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); (b) *ibid.*, **84**, 4527 (1962); (c) H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 1436 (1964); (d) *ibid.*, **89**, 906 (1967).

(4) All compounds analyzed satisfactorily. Complete synthetic and degradative details will be given in our full publication.

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

(6) Independently synthesized by R. L. Morse in these laboratories.

(7) Concerning the benzophenone–benzhydrol reaction, note W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(8) The similarity of the absorption spectrum of **2** to purely aliphatic models with the addition of weak isolated phenyl absorption suggests little ground-state conjugation. Thus methylenecyclohexadiene has been reported by H. Plieninger and W. Maier-Borst, *Chem. Ber.*, **98**, 2504 (1965), as absorbing at 242 m$\mu$. Compound **2** absorbs at 247 and 254 (sh) m$\mu$. However, as the rearrangement begins, overlap and distribution of the excitation must increase. Two chromophores with similar energies may interact especially strongly.