

Photochemical Rearrangement of 4-Aryl-Substituted Cyclopentenones. Low-Temperature Photochemistry and Direct Observation of Reaction Intermediates^{1,2}

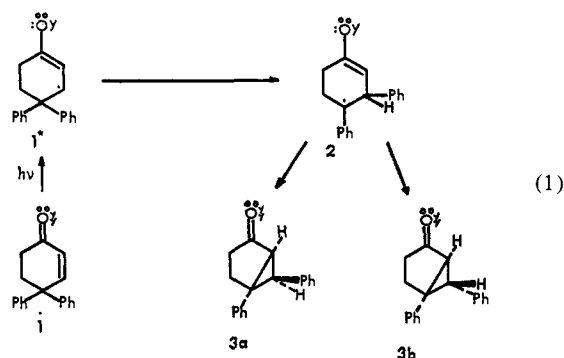
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Abstract: Irradiation of 4,4-diphenylcyclopentenone was shown to give a phenyl migration reaction leading to 3,4-diphenyl-4-pentenoic acid ketene. In *tert*-butyl alcohol, the corresponding ester was obtained. Similarly, photolysis of 4-methyl-4-phenylcyclopentenone gave 3-phenyl-4-methyl-4-pentenoic acid ketene in aprotic solvents and the *tert*-butyl ester in *tert*-butyl alcohol. The reaction efficiencies in *tert*-butyl alcohol were $\phi = 0.31$ and 0.55 respectively for the diphenyl and phenylmethyl enones. The rearrangements were shown by acetophenone sensitization and by cyclohexadiene quenching experiments to derive from the triplet excited state of the enones. At low temperature (-140°) a reaction intermediate was observed and assigned a bicyclo[2.1.0]pentane structure. The bicyclopentane was shown to proceed both photochemically and thermally to the ketene product observed at room temperature. Nonphotochemical approaches to the bicyclo[2.1.0]pentane, beginning with 1-diazo-*cis*-4,5-diphenylpent-4-en-2-one, were successful. Thus copper-bronze-catalyzed carbene generation led to an unstable species which on methanolysis gave methyl 3,4-diphenyl-4-pentenoate along with lesser products.

In view of the fascinating rearrangements uncovered in cyclohexenone photochemistry³ we thought it of considerable interest to determine if comparable photochemistry might occur in the case of cyclopentenones.

With the example of 4,4-diphenylcyclohexenone³ (1) in mind (note eq 1), 4,4-diphenylcyclopentenone and 4-methyl-4-phenylcyclopentenone were selected for study.



Synthesis of Cyclopentenone Reactants. In the case of 4,4-diphenylcyclopentenone our synthesis began with 5,5-diphenylcyclopent-2-en-1-one (4).⁴ This was found to afford 2,2-diphenylcyclopentanol (5) on sodium borohydride reduction in ethanol. The reduction of cyclopentenones to the saturated alcohol has precedent.⁵

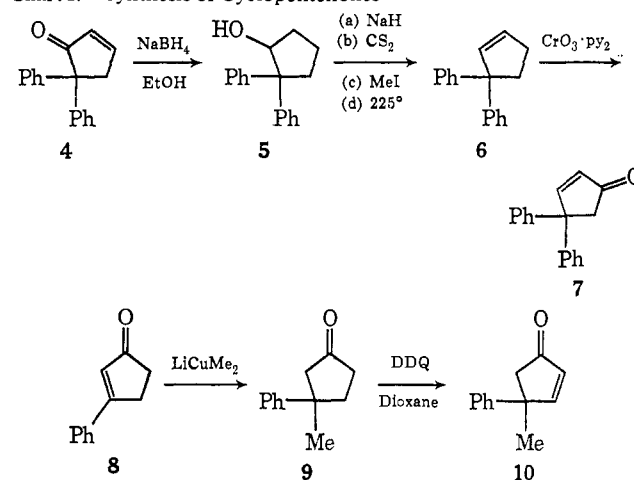
(1) Paper LXXXVII of Mechanistic and Exploratory Organic Photochemistry. For the previous paper of the series, note H. E. Zimmerman, *Tetrahedron*, 30, van't Hoff-LeBel Memorial Issue, June (1974).

(2) (a) A preliminary account of our results has been reported: H. E. Zimmerman and R. D. Little, *J. Chem. Soc., Chem. Commun.*, 698 (1972). (b) Also, related independent and concurrent studies of S. Wolff and W. C. Agosta, *ibid.*, 226 (1972), have been described.

(3) (a) H. E. Zimmerman and J. W. Wilson, *J. Amer. Chem. Soc.*, 86, 4036 (1964); (b) H. E. Zimmerman and K. G. Hancock, *ibid.*, 90, 3749 (1968); (c) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, 88, 1965 (1966); (d) H. E. Zimmerman and D. J. Sam, *ibid.*, 88, 4905 (1966); (e) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, 89, 2033 (1967); (f) H. E. Zimmerman and R. L. Morse, *ibid.*, 90, 954 (1968); (g) H. E. Zimmerman and N. Lewin, *ibid.*, 91, 879 (1969); (h) H. E. Zimmerman and W. R. Elser, *ibid.*, 91, 887 (1969).

(4) P. N. Craig and I. H. Witt, *J. Amer. Chem. Soc.*, 72, 4925 (1950).

Chart I. Synthesis of Cyclopentenones



Xanthate elimination and subsequent allylic oxidation afforded the desired 4,4-diphenylcyclopentenone (7). This sequence is indicated in Chart I and described in detail in the Experimental Section.

The preparation of 4-methyl-4-phenylcyclopentenone is also outlined in Chart I. This preparation started with 3-phenylcyclopentenone (8).⁶ Conjugate addition using lithium dimethylcuprate⁷ followed by dichlorodicyanoquinone oxidation⁸ led to the desired cyclopentenone 10.

Exploratory Photochemistry and Product Structure Elucidation. Photolysis of 4,4-diphenylcyclopentenone (7) in *tert*-butyl alcohol led to a solid, mp $85-86^\circ$, essentially quantitatively. This product showed *tert*-butoxyl absorption in the nmr at τ 8.67. Also the infrared possessed a band at 5.80μ as well as a broad band at 7.99μ suggesting⁹ that an ester, here a *tert*-butyl

(5) (a) H. C. Brown and H. M. Hess, *J. Org. Chem.*, 34, 2206 (1969); (b) P. R. Story and S. R. Fahrenholtz, *J. Amer. Chem. Soc.*, 89, 5633 (1967).

(6) W. Borsche and W. Menz, *Chem. Ber.*, 41, 190 (1908).

(7) (a) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, 31, 3128 (1966); (b) G. H. Posner, *Org. React.*, 19, 1 (1972).

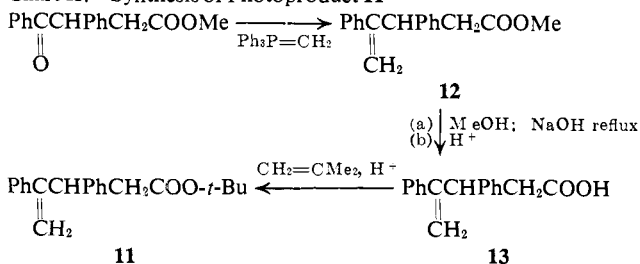
(8) E. A. Braude, A. G. Brook, and R. P. Linstead, *J. Chem. Soc., London*, 3569 (1954).

(9) K. Nakanishi, "Practical Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 24.

ester, was present. The nmr also revealed two vinyl hydrogens at τ 4.66 and 4.86, and the latter showed allylic (0.9 Hz) splitting. An intense infrared band at 11.21μ suggested⁹ the $=CH_2$ moiety. Coupled with the nmr and infrared evidence bearing on this grouping, we noted an intense ultraviolet band at 245 nm (ϵ 12,000). This provided evidence for the presence of a styryl group (*i.e.*, $PhC=CH_2$).¹⁰ The ten-hydrogen aryl absorption at τ 2.79 was compatible with the presence of two phenyl groups. Finally, three additional hydrogens absorbed in the nmr. One was a triplet at τ 5.61 implying a low-field methine possibly adjacent to a $-CH_2-$ group. This conclusion was in accord with a two-hydrogen multiplet at τ 7.25. With one of the two phenyl groups not yet allocated, the low field of the methine seemed most reasonably due to its being benzylic and probably also allylic, leading to $PhCHCH_2$ or $CH_2=C(Ph)CHPh-CH_2$ groupings.

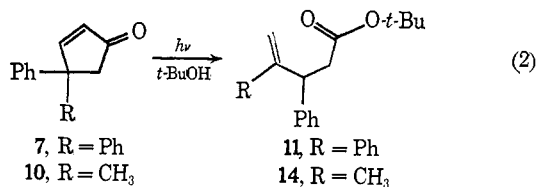
This reasoning led us to entertain structure **11** for the mp 85–86° photoproduct. Firm evidence confirming this view derived from the independent synthesis outlined in Chart II and detailed in the Experimental

Chart II. Synthesis of Photoproduct **11**



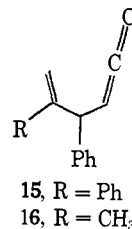
Section. This synthesis led to material identical with the photoproduct.

Similar exploratory irradiation of 4-methyl-4-phenylcyclopentenone (**10**) in *tert*-butyl alcohol led to a single photoproduct **14** whose spectral properties were similar to those of the diphenyl analog except for a new τ 8.39 broadened singlet expected if the styryl portion of the molecule **11** was replaced by $CH_3C=CH_2$ in the present photoproduct **14**. This example has also been reported by Agosta.^{2b} The over-all reaction can thus be pictured as in eq 2.



In a run with diphenylenone **7** using benzene solvent at room temperature, aliquots were withdrawn at intervals during 1 hr. Concentration and infrared analysis indicated a progressively increasing absorption at 4.74μ at the expense of the enone carbonyl stretching absorption at 5.86μ . At the end of the hour, methanol quenching led to the methyl ester **12** which was already in hand. This evidence in the form of typical ketene infrared absorption and the nature of the reaction with methanol leads to formulation of the photochemical rearrangement as proceeding *via* ketene **15** in the case

of the diphenylenone irradiation. Again there is agreement with the results of Agosta^{2b} who provided similar infrared evidence for the intervention of **16** in the photochemistry of **10**.



Quantum Yield and Multiplicity Studies. With evidence for the reaction course in hand,² we proceeded to investigate the mechanistic details of the reaction. Quantum yields for the diphenylenone **7** were determined using the Black Box apparatus described by us previously¹¹ using ferrioxalate actinometry¹² and solution filters. In the case of the methylphenylenone **10**, the semimicro optical bench described earlier¹¹ was employed. The quantum efficiency for product formation from diphenylenone in *tert*-butyl alcohol was $\phi = 0.31$ and that for methylphenylenone in the same solvent was $\phi = 0.55$. Acetophenone sensitization was carried out with diphenylenone giving a sensitized quantum yield of $\phi = 0.30$. Quenching was observed with 0.23 *M* cyclohexadiene to the extent of 16%. These results are compiled in Table I and detailed in the Experimental Section.

Table I. Quantum Yield Determinations

Reactant (concn) ^a	Additive	% conversion ^b	ϕ
Diphenylenone (1.70×10^{-3})	None	34	0.31
Diphenylenone (5.15×10^{-3})	None	16	0.30
Diphenylenone (1.65×10^{-3})	Acetophenone, 0.14 <i>M</i>	36	0.31
Methylphenylenone (1.53×10^{-2})	None	16	0.55
Diphenylenone (5.48×10^{-3})	Cyclohexadiene, 0.23 <i>M</i>	9.1	0.25

^a In *tert*-butyl alcohol solvent. ^b Assayed chromatographically with isolation.

Thus, it can be seen that the reaction of the two enones, **7** and **10**, is a quite efficient process. It is also clear that the rearrangement occurs from the triplet excited state to give the same product and with the same efficiency as in direct irradiation runs. Furthermore, it is apparent that the reaction is subject to quenching by the triplet energy acceptor, cyclohexadiene. For the sensitized quantum yield of diphenylenone **7** and the direct irradiations to give the same efficiency, we must conclude either that the quantum yields are fortuitously identical or more simply that the same excited state (*i.e.*, triplet) is responsible for both reactions. This also suggests that intersystem crossing is essentially of unit efficiency for diphenylcyclopentenone **7**, since otherwise a lower

(10) E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, New York, N. Y., 1955, p 153.

(11) H. E. Zimmerman, *Mol. Photochem.*, **3**, 281 (1971).
 (12) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. B*, **140**, 470 (1953).

efficiency would be observed in the nonsensitized runs. Finally, quenching does support this interpretation.

Low-Temperature Studies. Observation of Reaction Intermediates. From the results thus far obtained, the photochemistry of cyclopentenones **7** and **10** appeared to be quite different from that of rather similar cyclohexenones studied by us previously³ where bicyclo[3.1.0]hexane products were obtained. Also, in the case of cyclopentenones, there have been examples reported of bicyclo[2.1.0]pentan-2-ones being isolated as stable products.^{13,14} It was thought that at lower temperatures than the runs described above it might be possible to observe any bicyclic intermediates involved in the rearrangements.

Two types of low-temperature irradiations were carried out. One employed infrared monitoring of the photolysis with no attempt at isolation. These runs utilized a low-temperature infrared cell (note Experimental Section) allowing irradiation through sodium chloride at temperatures ranging from near liquid nitrogen to room temperature, followed by subsequent infrared measurement. A larger apparatus was constructed which allowed cooling of 22-ml samples to the desired low temperature and irradiation on a larger scale. This apparatus is described in the Experimental Section. We were thus able both to monitor infrared spectral changes during low-temperature irradiations and also to isolate the resulting materials after warming to room temperature.

The low-temperature photolyses were run at -140 to -120° in 1:1 THF-ether. Photolysis of diphenylenone **7** with relatively monochromatic light at 366 nm led to development of absorption at 5.67μ with loss of the enone carbonyl stretch at 5.86μ . This process could be carried very nearly to completion (*ca.* 80%; note Figure 1). When the monochromator was then reset to 315 nm, where a nonconjugated carbonyl would absorb in the ultraviolet, further irradiation resulted in development of a ketene absorption band at 4.74μ and to loss of the $5.67\text{-}\mu$ peak. In runs in which the 315-nm photolysis was omitted but in which the $5.67\text{-}\mu$ intermediate was allowed to warm to room temperature, the same conversion to ketene was encountered.

The spectroscopically monitored runs were paralleled by photolyses in the larger, preparative apparatus. Here the amount of light employed was adjusted by use of actinometry to the amount used in the spectroscopically monitored experiments. Irradiation at 366 nm followed by warming led to product which was then quenched with methanol. The products isolated proved to be methyl ester **12** along with smaller amounts of the corresponding acid **13**. The latter appeared to derive from adventitious water present in the methanol.

Some parallel studies were carried out starting with the methylphenylenone **10** and it was observed that a similar $5.71\text{-}\mu$ carbonyl absorption developed upon 366-nm irradiation at -140° . Again, subsequent photolysis at 315 nm led to ketene absorption at 4.74μ .

The $5.67\text{-}\mu$ and $5.71\text{-}\mu$ carbonyl absorptions are ascribed to a housone (*i.e.*, a bicyclo[2.1.0]pentan-2-one) carbonyl. A $5.67\text{-}\mu$ absorption band was reported for

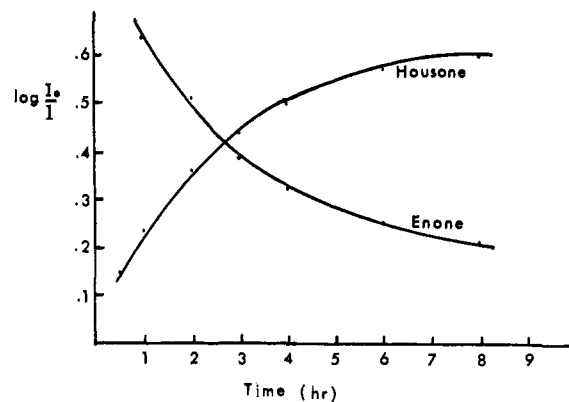
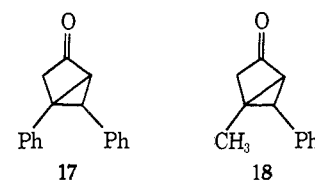


Figure 1. Relative concentrations of diphenylenone **7** and housone **17** as a function of time.

5-pivaloyl-1,3-di-*tert*-butylbicyclo[2.1.0]pentan-2-one by Matsuura and Ogura.^{13b} The low-temperature intermediates are assigned structures **17** and **18** on this basis

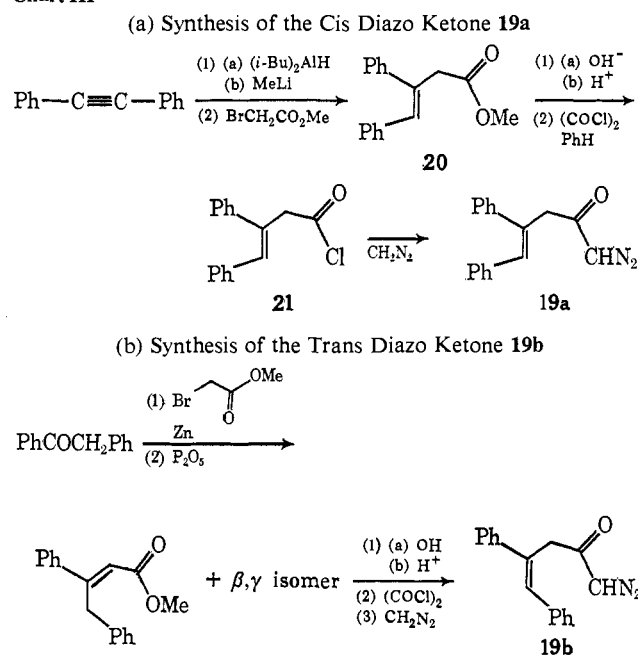


and on mechanistic grounds accounting for the formation and subsequent reactivity of such housones.

Nonphotochemical Entry to the Reaction Pathway. One thought which intrigued us was the possibility of either obtaining housone **17** without the use of light or alternatively generating biradical species which seemed likely to occur in the photochemical mechanism.

Our approach was aimed at the synthesis and reaction of diazo ketone **19** (note Charts IIIa and b) since

Chart III



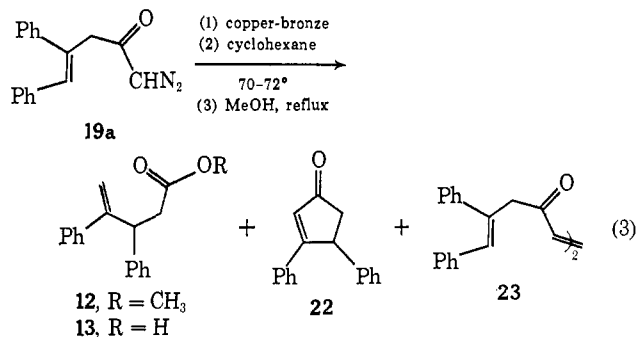
it was hoped that an internal carbenoid addition to the double bond would afford the desired housone. The trans diazo ketone **19b** did react under a variety of conditions, but there was no evidence for formation of

(13) (a) T. Matsuura and K. Ogura, *J. Chem. Soc., Chem. Commun.*, 1247 (1967); (b) *J. Amer. Chem. Soc.*, **89**, 3850 (1967).

(14) D. A. Plank and J. C. Floyd, *Tetrahedron Lett.*, 4811 (1971).

any product absorbing at short wavelength (*i.e.*, near 5.67μ) in the infrared.

More success was obtained with the *cis* diazo ketone **19a** where copper-bronze-catalyzed decomposition in cyclohexane led to an unstable product with an infrared absorption at 5.60μ ; this corresponded to approximately half of the reaction product. Numerous attempts to isolate this component on a wide variety of chromatographic supports were unsuccessful. On treatment with methanol at $65-70^\circ$ the already identified methyl ester **12** and its corresponding acid **13** were isolated in a total yield of 45%. Note eq 3. Additionally,



3,4-diphenylcyclopentenone (**22**) and dimer **23** were isolated in 17 and 3% yields, respectively. The remaining material appeared to consist of 15 (!) additional products in approximately equal quantities; thus no attempt was made to characterize these.

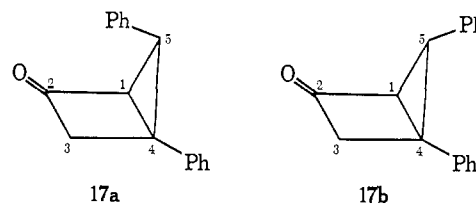
Thus, the attempt to generate housone **17** did lead to product with the carbonyl absorption in approximately the correct region of the infrared, and this product did react with methanol in a fashion parallel to that of the photoproduct. It is to be noted, however, that the carbonyl absorption was at slightly shorter wavelength and also that the housone photoproduct seemed to proceed to form unsaturated ketene **15** at lower temperatures than the intermediate presently generated. A reasonable conclusion, to be discussed subsequently, is that the photochemically and diazo ketone generated housones are stereoisomers.

Interpretative Discussion. The first point to be noted is that a phenyl migration process does occur as might be expected from cyclohexenone photochemistry.³ Thus, in each enone a phenyl group migrates to the β carbon of the enone moiety. The low-temperature behavior is exactly parallel to the cyclohexenone photochemistry (*i.e.*, in affording bicyclic ketone).

An additional similarity to cyclohexenone photochemistry is the triplet reaction multiplicity. The facile intersystem crossing observed presently for cyclopentenones also is reminiscent of cyclohexenone behavior.^{3b}

There is a stereochemical point of real interest. In the photochemical formation of housone **17** we would expect a kinetic preference for the *trans* stereoisomer **17a**, since this reaction stereochemistry is ubiquitously preferred in six-ring phenyl migrations.^{3,15} Con-

versely, one would expect¹⁸ the nonphotochemical diazo ketone approach to proceed stereospecifically and thus to give *cis*-housone **17b** since starting material has the *cis* configuration.

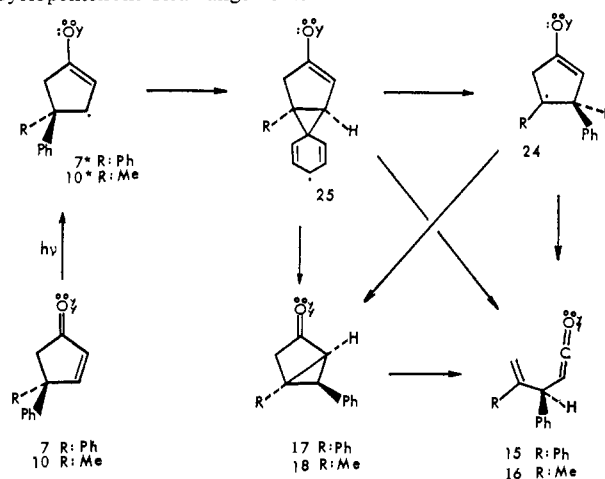


The occurrence of **17a** in the photochemical generation and **17b** from the nonphotochemical approach does rationalize the somewhat different thermal stabilities of the bicyclic system in the two approaches. The greater thermal stability of stereoisomer **17b** is most likely a result of the restricted rotation of the C-4 phenyl group as a consequence of a *cis*-C-5 phenyl. The C-4 phenyl must overlap with the internal σ bond to facilitate ring opening and cannot do so readily in the *cis* isomer. This effect has been considered earlier in connection with 4,4-diphenylcyclohexenone photochemistry.^{3b}

The mechanism of the diazoketone decomposition still has to be discussed. It seems likely that the initially generated carbene does successfully add, at least in part, to the *cis*-stilbenyl double bond to give *cis*-housone **17b**. Unsaturated ester **12** most likely arises from housone decomposition paralleling the thermal decomposition of photochemically generated housone **17a**.

Finally, in spite of the observation of the housone intermediate at low temperature, the question remains whether this is sufficient evidence that this is the mechanism followed in the room-temperature irradiations.¹⁹ Actually, although the evidence is suggestive it does not require the intervention of the housone intermediate at room temperature. In fact, reaction mechanisms may well be temperature dependent. In the present instance

Chart IV. Mechanisms of Disubstituted Aryl Cyclopentenone Rearrangements



(note Chart IV) if phenyl were to migrate to the β carbon of the excited enone moiety without concomitant three-

(15) Additionally this stereochemistry is observed in hydrocarbon six-ring photochemistry and in singlets and in triplets.^{16,17}

(16) H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **92**, 1411 (1970).

(17) H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **91**, 5307 (1969).

(18) (a) G. Stork and M. Marx, *J. Amer. Chem. Soc.*, **91**, 2371 (1969); (b) G. Stork and M. Gregson, *ibid.*, **91**, 2373 (1969); (c) M. M. Fawzi and C. D. Gutsche, *J. Org. Chem.*, **31**, 1390 (1966).

(19) The independent investigation^{2b} of the room-temperature photochemistry of 4-methyl-4-phenylcyclopentenone is in agreement with our own room-temperature findings.

ring formation, the biradical species **24** formed would be potentially capable of either collapsing to housone **17a** or proceeding directly to unsaturated ketene **15**. Additionally, at low temperature it is possible that phenyl-bridged species **25** may lead directly to the housone.

Thus, while it is perfectly possible that housone is formed independent of temperature and is just thermally unstable in the room-temperature runs, it is equally possible that an intermediate too unstable to survive at room temperature has a bond energy too weak to be formed under these conditions in the first place. Under conditions where the available vibrational energy exceeds the energy for formation of housone from biradical **24**, the existence of housone as an intermediate then is an esoteric question more semantic in nature than theoretical.

Experimental Section²⁰

2,2-Diphenylcyclopentanol. A solution of 3.50 g (15 mmol) of 5,5-diphenylcyclopent-2-en-1-one⁴ in 30 ml of ethanol was added dropwise to a stirred slurry of 1.14 g (30 mmol) of sodium borohydride in ethanol under nitrogen and the mixture was refluxed 1 hr, cooled, hydrolyzed using 3% sodium hydroxide, ether extracted, dried, and concentrated *in vacuo* to afford 3.42 g of essentially pure alcohol as a viscous oil. The alcohol was passed through a 50 × 8 cm 1:1 silica gel-Norit column using 1:2 ether in hexane to remove colored impurities and afforded 3.30 g (92%) of pure 2,2-diphenylcyclopentanol.

The spectral data were: ir (neat) 2.89, 3.26, 3.37, 6.27, 6.72, 6.91, 9.0, 9.33, 9.70, 9.88, 13.32, 14.31 μ ; nmr (CDCl₃) τ 8.47 (br s, 1 H, OH), 8.4–7.09 (m, 6 H, -CH₂-), 5.22 (m, 1 H, methine), 2.8 (s, 10 H, arom). The broad singlet at τ 8.47 disappeared upon the addition of 0.02 ml of deuterium oxide.

Anal. Calcd for C₁₇H₁₈O: C, 85.71; H, 7.56. Found: C, 85.67; H, 7.55.

3,3-Diphenylcyclopentene. To a dry, nitrogen purged flask was added 1.55 g (33.5 mmol) of sodium hydride (52% by weight in mineral oil) and 6.00 g (25.20 mmol) of 2,2-diphenylcyclopentanol in 120 ml of anhydrous ether. After 8.5 hr at reflux, 1.87 ml (31 mmol) of carbon disulfide in 60 ml of anhydrous ether was added. After another 10.25 hr, 1.95 ml (31 mmol) of methyl iodide in 100 ml of anhydrous ether was added. The mixture was refluxed for an additional 12 hr, cooled, water washed, dried, and concentrated *in vacuo* to afford 7.2 g of essentially pure yellow crystalline xanthate which was purified by trituration with ether to afford 7.0 g (85%) of pure xanthate. The infrared spectrum showed strong bands at 8.12, 8.39, 9.49, and 9.60 μ characteristic of xanthate esters.²¹ The nmr spectrum (CDCl₃) showed an *S*-methyl singlet at τ 7.90.

The xanthate was heated (no solvent) for 35 min at 210–235°. The residue was flushed with nitrogen, dissolved in carbon tetrachloride, concentrated *in vacuo*, and decolorized on a 50 × 8 cm 1:1 silica gel-Norit column using hexane as eluent. Distillation at 119–121° (0.1 mm) afforded 4.60 g (98%) of the desired 3,3-diphenylcyclopentene as a colorless liquid.

The spectral data were: ir (CCl₄) 3.28, 3.42, 6.29, 6.74, 6.97, 9.80, 13.30, 14.34 μ ; nmr (CCl₄) τ 7.52 (pseudo d, 4 H, -CH₂-), τ_A 3.92, τ_B 4.19 (AB q, 2 H, J_{AB} = 6.1 Hz, vinyl), 3.11 (s, 10 H, arom).

Anal. Calcd for C₁₇H₁₆: C, 92.73; H, 7.27. Found: C, 92.77; H, 7.17.

4,4-Diphenylcyclopentenone. The chromium trioxide-pyridine complex was prepared using the method of Dauben, *et al.*,²² and was stored in a vacuum desiccator over phosphorus pentoxide prior to use.

To a stirred solution of 17.60 g (68.10 mmol) of the chromium trioxide-pyridine complex in 200 ml of methylene chloride at room temperature under nitrogen was added 1.00 g (4.55 mmol) of 3,3-

diphenylcyclopentene in 75 ml of methylene chloride. A tarry black-brown precipitate separated within 5 min. The mixture was stirred at room temperature for 24 hr, the precipitate was ether washed, and the washings were combined with the methylene chloride and washed with saturated bicarbonate, ether extracted, washed with 5% HCl, 5% sodium bicarbonate, and saturated sodium chloride, and dried. Concentration *in vacuo* afforded 1.09 g of an oil which was chromatographed on a 3 × 109 cm Pyrex column slurry packed with silicic acid (Silicar CC-7) using 1:1 ether-hexane and washed with hexane. The eluent was scanned at 264 nm and 40-ml fractions were collected. Elution with 1.5 l. of hexane, 2 l. of 5%, 500 ml of 7%, and 2 l. of 10% ether in hexane gave: fractions 21–35, 0.395 g of 3,3-diphenylcyclopentene; fractions 110–125, 0.55 g of 4,4-diphenylcyclopentenone, mp 57–60°. Recrystallization from ether-hexane gave 0.522 g of 4,4-diphenylcyclopentenone (84% based on recovered starting material), mp 62–63°.

The spectral data were: ir (NaCl) 3.25, 3.29, 3.31, 3.40, 3.48, 5.86, 5.96 (sh), 6.30, 6.70, 6.94, 7.11, 7.28, 7.51, 7.79, 7.98, 8.40, 8.66, 8.79, 9.29, 9.51, 9.70, 10.00, 10.35, 11.05, 11.91, 12.61, 13.28, 14.35, 15.4 μ ; uv (95% EtOH) λ_{max} 318 (ϵ 47); nmr (CDCl₃) τ 6.95 (s, 2 H, -CH₂-), 3.84 (d, 1 H, J = 5.5 Hz, α -vinyl), 2.82 (s, 10 H, arom), 2.09 (d, 1 H, J = 5.5 Hz, β -vinyl).

Anal. Calcd for C₁₇H₁₄O: C, 87.18; H, 5.98. Found: C, 87.24; H, 6.07.

3-Methyl-3-phenylcyclopentanone. To a slurry of 6.00 g (31.6 mmol) of cuprous iodide in 50 ml of anhydrous ether cooled to -20° and purged with oxygen-free nitrogen²³ was added 13.2 ml of methyl lithium in ether (31.6 mmol, 2.4 *M*) *via* syringe. Then 1.25 g (7.92 mmol) of 3-phenylcyclopentenone in 76 ml of ether was added and the yellow mixture stirred at -20 to -50° for 20 hr, then brought to room temperature for 32.5 hr and finally poured into a saturated ammonium chloride solution and shaken vigorously. The solution was filtered, ether extracted, dried, and concentrated *in vacuo* to afford crude ketone which was decolorized on a 50 × 8 cm 1:1 silica gel-Norit column using ether to give 1.15 g of essentially pure ketone. Distillation at 79° (14 mm) afforded 1.05 g (76%) of pure 3-methyl-3-phenylcyclopentanone as a clear, colorless liquid.

The spectral data were: ir (NaCl) 3.25, 3.29, 3.37, 3.40, 3.47, 5.72, 6.69, 6.91, 7.11, 7.27, 7.60, 7.89, 8.68, 9.29, 9.70, 13.06, 13.29, 14.31 μ ; nmr (CDCl₃) τ 2.70 (s, 5 H, arom), 7.44 (br s, 1 H, C-2 -CH₂-), 7.52 (br s, 1 H, C-2 -CH₂-), 7.73 (br s, 4 H, C-4 and C-5 -CH₂-), 8.64 (s, 3 H, CH₃).

Anal. Calcd for C₁₂H₁₄: C, 82.76; H, 8.05. Found: C, 82.77; H, 8.11.

4-Methyl-4-phenylcyclopentenone. A solution of 1.31 g (7.55 mmol) of 3-methyl-3-phenylcyclopentanone and 1.88 g (8.30 mmol) of dichlorodicyanobenzoquinone in 78.0 ml of dry dioxane was refluxed for 38 hr, cooled, filtered, washed with 50% ether in pentane, washed with 1 *N* sodium hydroxide, dried, and concentrated *in vacuo*. The material was chromatographed on a 3 × 105 cm Vycor column slurry packed with silica gel (Grace, grade 62) in 1:2 ether-hexane and washed with hexane. Elution with 500 ml of hexane, 500 ml of 5% ether in hexane, and 1.5 l. of 7% and 3 l. of 10% ether in hexane gave nil; with 4 l. of 15% ether in hexane gave 1.0 g of starting material; and with 2 l. of 20% ether in hexane gave 0.250 g of 4-methyl-4-phenylcyclopentenone. Distillation at 60° (0.1 mm) afforded 0.212 g (16.4%) of the pure enone.

The spectral data were: ir (NaCl) 3.23, 3.26, 3.29, 3.36, 3.40, 3.47, 5.87, 6.01 (sh), 6.32, 6.71, 6.93, 7.1, 7.29, 7.47, 7.92, 8.31, 8.60, 9.30, 9.51, 9.75, 11.00, 12.00, 12.48, 13.18, 13.74, 14.35, 15.50 μ ; nmr (CDCl₃) τ 8.42 (s, 3 H, CH₃), 7.44 (s, 2 H, -CH₂-), 3.86 (d, 1 H, J = 5.8 Hz, α -vinyl), 2.74 (s, 5 H, arom), 2.36 (d, 1 H, J = 5.8 Hz, β -vinyl).

Anal. The mass spectrum (70 eV) showed a molecular ion at *m/e* 172.0888. Calcd for C₁₂H₁₂O: 172.0890. Calcd for C₁₂H₁₂O: C, 83.72; H, 6.98. Found: C, 83.61; H, 6.85.

Methyl 3,4-Diphenyl-4-pentenoate. To a solution of methyl-enetriphenylphosphorane prepared from 1.11 g (3.18 mmol) of methyltriphenylphosphonium bromide and 1.20 ml (3.18 mmol) of *n*-butyllithium in hexane was added 900 mg (3.52 mmol) of methyl 3,4-diphenyl-4-oxobutanoate²⁴ in 2.0 ml of anhydrous ether. After stirring for 17 hr at room temperature, the mixture was filtered, water washed, dried, and concentrated *in vacuo*. The material was chromatographed on a 2.5 × 99 cm Vycor column slurry packed with silica gel using 1:3 ether-hexane and washed with

(20) All melting points were taken on a hot-stage apparatus calibrated with known compounds.

(21) T. Taguchi and M. Nakao, *Tetrahedron*, **18**, 245 (1962).

(22) (a) W. G. Dauben, M. Lorber, and D. S. Fullerton, *J. Org. Chem.*, **34**, 3587 (1969); (b) see also J. C. Collins, *Tetrahedron Lett.*, 3363 (1968).

(23) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

(24) E. Knoevenagel, *Chem. Ber.*, **21**, 1350 (1888).

hexane. Elution with 500 ml of hexane, 250 ml of 1% ether in hexane, 250 ml of 2%, and 500 ml of 5% ether in hexane all afforded no material; with 4 l. of 6% afforded 135 mg of the starting keto ester; with 500 ml of 8%, 1 l. of 10%, and 1.5 l. of 15% ether in hexane afforded nil; and with 1.5 l. of 25% ether in hexane gave 350 mg of the desired vinyl ester. Distillation at 79° (1.6 mm) afforded 300 mg (32%) of pure methyl 3,4-diphenyl-4-pentenoate.

The spectral data were: ir (neat) 3.24, 3.26, 3.29, 3.38, 3.42, 3.52, 5.78, 6.18, 6.29, 6.39, 6.74, 7.00, 8.04, 8.30, 8.68, 9.06, 9.34, 9.82, 11.15, 11.99, 12.91, 13.31, 14.39 μ ; nmr (CDCl₃) τ 2.79 (s, 10 H, arom), 4.84 (s, 1 H, vinyl), 4.61 (s, 1 H, vinyl), 5.52 (t, 1 H, $J = 8.0$ Hz, benzylic), 6.50 (s, 3 H, CH₃CO₂), 7.15 (m, 2 H, $J_{23} = 8.0$ Hz, $J_{2'3'} = 7.5$ Hz, -CH₂-).

Anal. Calcd for C₁₅H₁₈O₂: C, 81.20; H, 6.77. Found: C, 81.44; H, 6.85.

3,4-Diphenyl-4-pentenoic Acid. A solution of 50.0 mg (0.19 mmol) of methyl 3,4-diphenyl-4-pentenoate and 80.0 mg of sodium hydroxide in 30 ml of methanol was stirred at reflux for 1 hr. The mixture was cooled to 0°, acidified with 6 N hydrochloric acid, ether extracted, dried, concentrated *in vacuo*, and chromatographed on a 20 × 20 cm thick layer silica gel plate eluted with 10% ether in hexane to afford 39.1 mg of the desired acid. Recrystallization from ether gave 35.0 mg (73%) of 3,4-diphenyl-4-pentenoic acid, mp 161.5–162.5°.

The spectral data were: ir (CHCl₃) 2.80–4.20 (br), 5.85, 6.26, 6.70, 6.92, 7.09, 7.72, 8.22, 8.70, 9.02, 9.31, 9.72, 11.06, 13.30, 14.32, 15.00 μ ; nmr (CDCl₃) τ 2.79 (s, 10 H, arom), 4.66 (s, 1 H, vinyl), 4.86 (br s, 1 H, $J_{\text{allylic}} = 0.9$ Hz, vinyl), 5.60 (br t, 1 H, $J_{23} = 8.0$ and 7.5 Hz, benzylic), 7.15 (m, 2 H, -CH₂-).

tert-Butyl 3,4-Diphenyl-4-pentenoate. Isobutylene (ca. 20 ml) was condensed at -78° and added to a solution of 30.0 mg (0.12 mmol) of 3,4-diphenyl-4-pentenoic acid in 30 ml of ether containing 0.05 ml of concentrated sulfuric acid at -10°. The solution was stirred for 10 hr at -10°, warmed to room temperature, water washed, ether extracted, dried, and concentrated *in vacuo* to afford 16.2 mg of essentially pure *tert*-butyl ester. Recrystallization from benzene gave 15.5 mg (42%) of *tert*-butyl 3,4-diphenyl-4-pentenoate, mp 85–86°.

The spectral data were: ir (CHCl₃) 3.22, 3.25, 3.29, 3.35, 3.41, 5.80, 6.18, 6.26, 6.71, 7.18, 7.32, 7.99, 8.78, 9.31, 9.75, 11.21, 11.91, 12.89, 13.39, 14.36 μ ; nmr (CDCl₃) τ 2.79 (s, 10 H, arom), 4.66 (s, 1 H, vinyl), 4.86 (br s, 1 H, $J_{\text{allylic}} = 0.9$ Hz, vinyl), 5.61 (br t, 1 H, $J_{23} = 8.0$ Hz, $J_{2'3'} = 7.5$ Hz, benzylic), 7.25 (m, 2 H, -CH₂-), 8.67 (s, 9 H, *t*-Bu).

Anal. Calcd for C₂₁H₂₄O₂: C, 81.82; H, 7.79. Found: C, 81.65; H, 7.58.

trans-3,4-Diphenyl-3-butenic Acid Chloride. *trans*-3,4-Diphenyl-3-butenic acid, mp 172.5–173.0°, was prepared using the method of Kon and Nargard.²⁵ To a solution of 2.00 g (8.40 mmol) of the acid in 40 ml of benzene was added 1.43 ml (16.9 mmol) of oxalyl chloride in 10 ml of benzene and 0.10 ml of dimethylformamide. The mixture was stirred at room temperature for 45 min and concentrated *in vacuo* to afford 1.93 g (90%) of the desired acid chloride which was used immediately without further purification.

The spectral data were: ir (CDCl₃) 3.22, 3.25, 3.28, 3.34, 3.40, 5.58, 5.98, 6.23, 6.34, 6.69, 6.90, 7.09, 7.41, 7.68, 7.88, 8.08, 8.40, 9.29, 9.49, 9.69, 9.78, 9.98, 10.40, 11.19, 11.98, 12.69, 14.40, 15.47 μ ; nmr (CDCl₃) τ 5.83 (s, 2 H, -CH₂-), 2.93 (s, 1 H, vinyl), 2.64 (m, 10 H, arom).

1-Diazo-trans-4,5-diphenylpent-4-en-2-one. To a cold (0°) ethereal solution of distilled diazomethane prepared from 5.71 g of EXR-101 (70% *N,N'*-dimethyl-*N,N'*-dinitrosoterephthalamide in mineral oil) and 75 ml of 30% sodium hydroxide was added 1.10 g (4.30 mmol) of *trans*-3,4-diphenyl-3-butenic acid chloride in 10 ml of ether. After stirring 1 hr at room temperature, the excess diazomethane was removed in a nitrogen stream and the solvent was removed *in vacuo* to afford 1.00 g (90%) of the desired *trans* diazo ketone which was used without further purification.

The spectral data were: ir (CHCl₃) 3.20, 3.24, 3.28, 3.32, 3.41, 4.74 (strong), 5.80, 6.13 (strong), 6.71, 6.94, 7.09, 7.40, 7.74, 8.75, 9.30, 9.71, 10.61, 10.91, 11.53, 12.00, 14.41 μ ; nmr (CDCl₃) τ 6.27 (s, 2 H, -CH₂-), 4.76 (s, 1 H, CHN₂), 2.93 (s, 1 H, vinyl), 2.65 (br s, 10 H, arom).

Methyl cis-3,4-Diphenyl-3-butenate. Diisobutylaluminum hydride (37.40 ml, 56.10 mmol) was added to a solution of 10.00 g (56.10 mmol) of diphenylacetylene in 74 ml of hexane under nitrogen. The solution was stirred for 4 hr at 50–55° and cooled to

-30°, and 25.5 ml (56.1 mmol, 3.3 M) of methyl lithium in ether was added. The solution was stirred for 30 min and warmed to -10°, and 10.40 g (67.50 mmol) of methyl α -bromoacetate was added. The mixture was stirred at room temperature for 12 hr, refluxed 4 hr, cooled to -5 to 10°, washed using cold (0°) 3 N hydrochloric acid, ether extracted, washed with 10% sodium bicarbonate and saturated sodium chloride, dried, and concentrated *in vacuo*.

The material was chromatographed on a 105 × 3 cm Pyrex column slurry packed with silica gel in hexane. The eluent was scanned at 263 nm; 40-ml fractions were collected. Elution with 2.5 l. of hexane, 3.5 l. of 1% ether in hexane, and 4.0 l. of 5% ether in hexane gave: fractions 20–70, 220 mg of a mixture of diphenylacetylene and *cis*-stilbene; fractions 132–144, 145 mg of methyl *trans*-3,4-diphenyl-3-butenate; fractions 145–171, 1.822 g of methyl *cis*-3,4-diphenyl-3-butenate, mp 52–57°. Recrystallization of the *cis* ester from ether and trituration with cold hexane (0°) gave 1.749 g (12.4%) of pure *cis* ester, mp 58.5–60.0°.

The spectral data were: ir (CHCl₃) 3.23, 3.27, 3.30, 3.38, 3.41, 3.52, 5.78, 6.29, 6.38, 6.99, 7.10, 7.50, 7.92, 8.26, 8.39, 8.62, 9.26, 9.34, 9.46, 10.00, 10.58, 10.92, 11.11, 11.69, 12.85, 13.20, 13.69, 14.40, 15.20 μ ; nmr (CDCl₃) τ 6.58 (s, 2 H, -CH₂-), 6.51 (s, 3 H, OMe), 3.48 (s, 1 H, vinyl), 3.06 (s, 5 H, arom), 2.87 (s, 5 H, arom).

Anal. Calcd for C₁₇H₁₆O: C, 80.95; H, 6.35. Found: C, 80.55; H, 6.41.

cis-3,4-Diphenyl-3-butenic Acid. A solution of 1.20 g (47.60 mmol) of methyl *cis*-3,4-diphenyl-3-butenate and 1.90 g (47.60 mmol) of sodium hydroxide in 20 ml of methyl alcohol was refluxed for 2 hr and then cooled to -5°. The solution was acidified with cold (0°) 3 N HCl, ether extracted, dried, concentrated *in vacuo*, decolorized, and triturated with ether to afford 0.964 g (85%) of colorless, crystalline acid, mp 134.5–136.0°.

The spectral data were: ir (CHCl₃) 2.78–4.60 (br), 3.26 and 3.41, 5.82, 6.28, 6.38, 6.71, 6.95, 7.12, 7.80, 8.89, 9.36, 9.80, 10.57, 10.91, 11.58, 14.51, 15.10 (sh) μ ; nmr (CDCl₃) τ 6.48 (s, 2 H, -CH₂-), 3.40 (s, 1 H, vinyl), 2.96 (s, 5 H, arom), 2.88 (s, 5 H, arom).

cis-3,4-Diphenyl-3-butenic Acid Chloride. To 1.10 g (4.70 mmol) of *cis*-3,4-diphenyl-3-butenic acid in 50 ml of benzene containing a suspension of 1.01 g (9.52 mmol) of anhydrous sodium carbonate was added 0.81 ml (9.52 mmol) of oxalyl chloride and, after cooling at 0°, 0.05 ml of dimethylformamide. After stirring at 0° for 5 min and at room temperature for 5 min, the mixture was filtered and concentrated *in vacuo* to afford 0.96 g (86%) of the desired acid chloride which was used without further purification.

The spectral data were: ir (CHCl₃) 3.23, 3.26, 3.29, 3.32, 3.39, 3.41, 3.49, 5.60, 6.01, 6.29, 6.39, 6.73, 7.70, 7.86, 8.61, 9.32, 9.81, 10.49, 10.91, 11.55, 12.00, 14.80 (br), 15.63 μ ; nmr (CDCl₃) τ 6.06 (s, 2 H, -CH₂-), 3.47 (s, 1 H, vinyl), 3.04 (s, 5 H, arom), 2.87 (s, 5 H, arom).

1-Diazo-cis-4,5-diphenylpent-4-en-2-one. To a cold (0°) ethereal solution of distilled diazomethane prepared from 5.71 g of EXR-101 (70% *N,N'*-dimethyl-*N,N'*-dinitrosoterephthalamide in mineral oil) and 75 ml of 30% sodium hydroxide was added 1.20 g (4.69 mmol) of *cis*-3,4-diphenyl-3-butenic acid chloride in 10 ml of ether. After stirring 1 hr at room temperature, the excess diazomethane was removed under a stream of nitrogen and the solvent was removed *in vacuo*. Trituration of the initially formed crystals with ether afforded 1.21 g (98%) of the desired diazoketone, mp 78.0–79.5°.

The spectral data were: ir (CHCl₃) 3.20, 3.24, 3.27, 3.30, 3.33, 3.44, 3.50, 4.73 (strong), 6.16 (strong), 6.71, 6.97, 7.41 (strong), 7.74, 8.82, 9.11, 9.30, 9.80, 10.66, 10.92, 14.46, 15.18 (sh) μ ; nmr (CDCl₃) τ 6.51 (s, 2 H, -CH₂-), 4.74 (s, 1 H, CHN₂), 3.40 (s, 1 H, vinyl), 2.95 (br s, 5 H, arom), 2.77 (br s, 5 H, arom); mass spectrum *m/e* 262.

Anal. Calcd for C₁₇H₁₄N₂O: C, 77.86; H, 5.34. Found: C, 77.61; H, 5.51.

Copper-Catalyzed Decomposition of 1-Diazo-cis-4,5-diphenylpent-4-en-2-one. A solution containing 200.0 mg of copper-bronze (Luco brand, No. 16, Leo Uhlfelder, 99.5% copper) and 255.8 mg (0.978 mmol) of 1-diazo-*cis*-4,5-diphenylpent-4-en-2-one in 10 ml of cyclohexane was immersed in an oil bath preheated to 70–72° and stirred for 20 min. The mixture was cooled, filtered, and concentrated *in vacuo* to afford 12.1 mg of a yellow solid, mp 135.0–138.5°, which was removed by filtration and characterized as a diacetylene dimer (*vide infra*). The pea-green mother liquor, which showed an infrared carbonyl absorption at 5.60 μ (ca. 45% of the mixture), was dissolved in 30 ml of methanol, stirred under nitrogen at 65–70° for 30 min, water washed, ether extracted, dried, and concentrated *in vacuo* to afford a yellow oil which was im-

(25) G. A. R. Kon and K. S. Nargard, *J. Chem. Soc., London*, 2461 (1932).

mediately chromatographed on a 2.5×90 cm Pyrex column slurry packed with silica gel in hexane. The eluent was scanned at 264 nm and 40-ml fractions were collected. Elution with 3 l. of hexane, 2.5 l. of 1% ether in hexane, 1.5 l. of 2%, 1 l. of 4%, 1 l. of 8%, 1 l. of 10%, 3 l. of 15%, 1 l. of 20%, 1 l. of 25%, 1 l. of 50% ether in hexane, 2 l. of ether, and 1 l. of methyl alcohol gave: fractions 127–158, 65.7 mg of methyl 3,4-diphenyl-4-pentenoate characterized previously (*vide supra*); fractions 159–201, 20.0 mg of a four-component unidentified mixture; fractions 202–230, 19.4 mg of a two-component unidentified mixture; fractions 231–263, 23.6 mg of 3,4-diphenylcyclopent-2-en-1-one, mp 104.0–105.5° (*vide infra*); fractions 264–306, 23.7 mg of a three-component unidentified mixture; fractions 332–340, 11.3 mg (unidentified compound); fractions 384–390, 9.2 mg (unidentified compound); fractions 405–522, 48.3 mg of 3,4-diphenyl-4-pentenoic acid, mp 161.5–162.5°, characterized previously (*vide supra*).

The yellow solid, mp 135.0–138.5°, isolated prior to methanolysis (*vide supra*), was recrystallized from ether to give 8.2 mg of 1,2,9,10-tetraphenyldeca-1,5,9-triene-4,7-dione, mp 138–139°.

The spectral data were: ir (CHCl_3) 3.28, 3.30, 3.38, 3.42, 3.51, 5.91, 6.28, 6.38, 6.71, 6.94, 7.59, 7.88, 8.50, 9.20, 9.75, 10.79, 11.25, 14.56 μ ; nmr (CDCl_3) τ 6.46 (s, 4 H, $-\text{CH}_2-$), 3.49 (s, 2 H, vinyl), 2.80 (m, 24 H, arom); mass spectrum *m/e* 468.

Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_2$: C, 87.18; H, 5.98. Found: C, 87.50; H, 6.45.

3,4-Diphenylcyclopent-2-en-1-one was independently synthesized using the procedure of Japp and Landler²⁶ and afforded material identical with that obtained from decomposition of the diazo ketone (*vide supra*). The spectral data were: ir (CHCl_3) 3.26, 3.30, 3.32, 3.42, 5.89, 5.99, 6.30, 6.40, 6.71, 6.93, 7.12, 7.50, 7.57, 7.69, 7.90, 8.48, 9.32, 9.74, 10.64, 11.65, 14.39, 14.60 μ ; nmr (CDCl_3) τ 2.57 (m, 5 H, C-3 Ph), 2.83 (s, 5 H, C-4 Ph), 5.36 (C portion of an ABC pattern, 1 H, PhCH), 7.13 (AB portion of an ABC pattern, 2 H, $-\text{CH}_2-$), 3.28 (br s, 1 H, vinyl).

Purification of Benzene for Photolysis. Benzene (Mallinckrodt, reagent grade) was stirred with concentrated sulfuric acid (80 ml of sulfuric acid per liter of benzene) for 30 min. The yellow acid layer was removed and the process repeated three times. The benzene was washed with water and aqueous sodium bicarbonate, dried over magnesium sulfate, and distilled from lithium aluminum hydride onto molecular sieves (Fisher 4A sieve).

Exploratory Photolysis of 4,4-Diphenylcyclopentenone at Room Temperature. A degassed solution of 300 mg of 4,4-diphenylcyclopentenone in 200 ml of *tert*-butyl alcohol (6.4×10^{-3} M) under deoxygenated nitrogen²³ was photolyzed for 100 min using a 450-W Hanovia medium-pressure lamp equipped with a Pyrex filter. The *tert*-butyl alcohol was removed *in vacuo* and the resulting oil was chromatographed on a 77.5×2.5 cm Vycor column slurry packed with silica gel in ether and washed with 1:1 ether-hexane. Elution with 325 ml of 50% and 325 ml of 75% ether in hexane gave 273.9 mg of *tert*-butyl 3,4-diphenyl-4-pentenoate, mp 85–86°, after recrystallization from benzene; 1 l. of methanol gave 88 mg of 3,4-diphenyl-4-pentenoic acid, mp 161.5–162.5°, after recrystallization from ether. Both the ester and the acid were identical with independently synthesized material (*vide supra*).

Photolysis of 4,4-Diphenylcyclopentenone. Detection of a Ketene Intermediate. A solution of 300 mg of 4,4-diphenylcyclopentenone in 200 ml of benzene (6.4×10^{-3} M) was irradiated under the conditions described above. The reaction was monitored *via* ir by withdrawing 1.0-ml aliquots after 6, 21, 40, and 57 min irradiation. A band of 4.74 μ increased in intensity at the expense of the enone carbonyl absorption at 5.86 μ . After 66 min irradiation, the benzene was removed *in vacuo* and 50 ml of methanol was added. The solution was stirred for 100 min, water washed, ether extracted, dried, concentrated *in vacuo*, and chromatographed on a 78×2.5 cm Vycor column slurry packed with silica gel in hexane. Elution with 150 ml of hexane and 1 l. of 3%, 4 l. of 5%, and 1 l. of 10% ether in hexane gave 125 mg (0.535 mmol) of 4,4-diphenylcyclopentenone, mp 62–63°; 3.5 l. of 15% ether in hexane gave 230 mg (0.745 mmol) of methyl 3,4-diphenyl-4-pentenoate identical with an independently synthesized sample (*vide supra*).

Exploratory Photolysis of 4-Methyl-4-phenylcyclopentenone at Room Temperature. A degassed solution of 70.7 mg of 4-methyl-4-phenylcyclopentenone in 250 ml of *tert*-butyl alcohol (2.05×10^{-4} M) under deoxygenated nitrogen²³ was photolyzed for 1.0 hr using a 450-W Hanovia medium-pressure lamp equipped with a

Pyrex filter. Concentration *in vacuo* afforded 96.6 mg of *tert*-butyl 3-phenyl-4-methyl-4-pentenoate after decolorizing with Norit.

The spectral data were: ir (NaCl) 3.23, 3.25, 3.28, 3.34, 3.39, 5.79, 6.08, 6.24, 6.69, 6.89, 7.18, 7.31, 7.64, 7.96, 8.49, 8.75, 9.26, 9.73, 10.47, 11.21, 11.87, 13.31, 14.32 μ ; nmr (CDCl_3) τ 8.66 (s, 9 H, *t*-Bu), 8.39 (br s, 3 H, CH_3), 7.22 (m, 2 H, $J_{2,3} = 7.0$ Hz, $J_{2,4} = 8.0$ Hz, $-\text{CH}_2-$), 6.25 (t, 1 H, $J = 8$ Hz, benzylic), 2.78 (s, 5 H, arom).

Photolysis Equipment and Quantum Yield Determinations. Quantum yield irradiations of 4,4-diphenylcyclopentenone were performed on the Black Box apparatus¹¹ while those for 4-methyl-4-phenylcyclopentenone were performed on the micro optical bench.¹¹ Light output was monitored by ferrioxalate actinometry¹² and the light absorbed in the reaction cell was determined by the splitting ratio technique previously described.¹¹ For the Black Box irradiations, solution filters were used (*vide infra*). For the micro optical bench runs, the monochromator inlet slit was set at 5.4 mm and the exit slit at 3 mm giving a band pass of 22 nm at half-peak height.

Two filter solution systems were used for the Black Box irradiations. Nickel sulfate hexahydrate and cobalt sulfate heptahydrate in 10% sulfuric acid and stannous chloride dihydrate in 10% hydrochloric acid were used in preparing the filter solutions. Combination I: (2.4 cm thickness for each of the three cells) cell 1, 90.0 g of nickel salt per liter; cell 2, 200.0 g of cobalt salt per liter; cell 3, 10.2 g of tin salt per liter. The transmission curve for this combination displayed a maximum of 44% transmission at 325 nm, 0% at 295 nm, 25% at 310 nm, 36% at 315 nm, 22% at 350 nm, and 0% at 370 nm. Combination II: cell 1, 450.0 g of nickel salt per liter; cell 2, 281.0 g of cobalt salt per liter; cell 3, 3.50 g of tin salt per liter. The transmission curve for this combination displayed a maximum of 28% transmission at 323 nm, 10% at 340 nm, 1% at 350 nm, and 0% between 360 and 570 nm.

The photolysate was subjected to liquid-liquid partition chromatography on a 4×135 cm thermostated column of Celite (Eagel-Picher FW 80) which had been dry packed in the lower phase from 1 l. of cyclohexane, 400 ml of dimethylformamide, 250 ml of ethyl acetate, and 30 ml of water; the upper phase from this system was the eluent. The eluent was scanned at 260 nm; 40-ml fractions were collected.

Summary of Quantum Yields. The data are reported as follows: filter combination or monochromator setting, volume of *tert*-butyl alcohol solvent, starting enone, added reagent if any, light absorbed, product, quantum yield, per cent conversion.

Run 1. Combination 1, 750 ml, diphenyleneone (1.28 mmol), 2.0 mEinstein, diphenyl *tert*-butyl ester (0.620 mmol), $\phi = 0.31$, 34%.

Run 2. Combination 1, 750 ml, diphenyleneone (3.86 mmol), 2.03 mEinstein, diphenyl *tert*-butyl ester (0.617 mmol), $\phi = 0.30$, 16%.

Run 3. Combination 2, 750 ml, diphenyleneone (1.24 mmol), acetophenone (103.2 mmol), 2.0 mEinstein, diphenyl *tert*-butyl ester (0.623 mmol), $\phi = 0.31$, 36%.

Run 4. 313 nm, 39 ml, methylphenyleneone (0.598 mmol), 0.168 mEinstein, methyl phenyl *tert*-butyl ester (0.091 mmol), $\phi = 0.55$, 16%.

Run 5. 313 nm, 39 ml, diphenyleneone, (0.214 mmol), cyclohexadiene (0.23 M), 7.75×10^{-2} mEinstein, diphenyl *tert*-butyl ester (1.94×10^{-2} mmol), $\phi = 0.25$, 9.1%.

Purification of Solvents for Low-Temperature Photolysis. Tetrahydrofuran was refluxed over and distilled from lithium aluminum hydride immediately prior to use. Fresh cans of Mallinckrodt anhydrous ether were used without additional purification.

Small Scale Low-Temperature Infrared Photolysis Apparatus. A Beckman VLT-2 variable-temperature infrared unit (catalog No. 195793) was used in conjunction with an Osram HBO-200 super-pressure photolysis lamp focused with a Bausch and Lomb high-intensity monochromator. The monochromator inlet slit was set at 5.4 mm and the exit slit at 3 mm giving a band pass of 22 nm at half-peak height. The reaction was monitored using a Perkin-Elmer Infracord Model 137 spectrophotometer. The Beckman FH-01 sodium chloride cell, path length 0.1 mm and cell volume 0.038 ml, is drilled to accept an iron-constantan thermocouple so that the temperature of the cell can be measured at a point 1.5 mm from the sample. The thermocouple was calibrated using solid carbon dioxide at its sublimation temperature (-78.5°) as the reference point and afforded a smooth curve from which the emf value (millivolts) could be used to determine the operating temperature.

Preparative Scale Low-Temperature Photolysis Apparatus. The preparative scale apparatus is essentially a large scale version of the Beckman apparatus described above with the major exception

(26) F. R. Japp and G. D. Landler, *J. Chem. Soc., London*, 71, 123 (1897).

being that the reaction cannot be monitored by ir. The stainless steel cell has a 22-ml capacity and has been constructed using quartz end plates rather than sodium chloride as is used for the smaller apparatus.

Infrared Monitored Photolysis of 4,4-Diphenylcyclopentenone at Low Temperature. Irradiations were carried out using the micro-bench¹¹ and the small scale low-temperature photolysis apparatus described above. Solutions of 4,4-diphenylcyclopentenone or 4-methyl-4-phenylcyclopentenone in 1:1 ether-tetrahydrofuran were irradiated at $-140 \pm 5^\circ$. Typically, a 0.4 M solution of enone dissolved in 1:1 ether-tetrahydrofuran was added to the reaction cell and after evacuation of the surrounding chamber the cell was cooled to -140° and photolysis was initiated. Photolysis of the diphenylone (0.4 M) at -140° using 366-nm light was monitored over 930 min. During this time a new band appeared at 5.67μ and increased in intensity until the housone comprised ca. 80% of the photomixture at the expense of the enone carbonyl absorption at 5.86μ . There was no sign of ketene absorption at 4.74μ . The irradiation wavelength was then changed from 366 to 315 nm and photolysis was continued at -140° . The band at 5.67μ (housone) was converted to a band at 4.74μ (ketene) over a period of 5 hr of irradiation. The light flux was 0.119 mEinstein/hr.

Low-Temperature Photolysis of 4-Methyl-4-phenylcyclopentenone. Irradiation of 4-methyl-4-phenylcyclopentenone (0.40 M) in 1:1 ether-tetrahydrofuran for 100 min at -140° using 366-nm light afforded a new absorption at 5.71μ (housone) at the expense of the enone absorption at 5.87μ . There was no sign of ketene absorption at 4.74μ . When the wavelength was changed to 315 nm and the photolysis continued for 200 min at -140° , the $5.71\text{-}\mu$ band was converted to a band at 4.74μ (ketene). The light flux was 0.121 mEinstein/hr. This behavior closely parallels that of diphenylone (*vide supra*).

Infrared Monitored Photolysis of 4,4-Diphenylcyclopentenone. Photolysis at Low Temperature and Warming to Room Temperature.

A 0.4 M solution of 4,4-diphenylcyclopentenone in 1:1 ether-tetrahydrofuran was irradiated at 366 nm and -140° using the apparatus described above. After 8.0 hr, ir spectroscopy indicated that the housone absorption at 5.67μ had increased to ca. 70% of the photomixture at the expense of the enone absorption at 5.86μ . Irradiation was terminated and the reaction mixture was allowed to warm to room temperature while being monitored by ir. As the warming proceeded, the housone absorption at 5.67μ disappeared in a thermal process which converted it to the ketene band at 4.74μ .

Preparative Photolysis of 4,4-Diphenylcyclopentenone at Low Temperature. Isolation of Methyl 3,4-Diphenyl-4-pentenoate and 3,4-Diphenyl-4-pentenoic Acid upon Warming to Room Temperature. A solution of 4,4-diphenylcyclopentenone (109.1 mg, 0.466 mmol) in 22 ml of 1:1 ether-tetrahydrofuran was irradiated using the large scale photolysis apparatus described above. Potassium ferrioxalate actinometry¹² was used to determine that the light flux was 0.133 mEinstein/hr.

After cooling to -120° , photolysis was initiated. On termination of photolysis (24 hr), the solution was warmed to room temperature, removed from the photolysis cell, quenched with methanol, ether extracted, dried, and concentrated *in vacuo* to afford 98.7 mg of material. Preparative thick layer chromatography on a 20×20 cm silica gel plate eluted three times using 10% ether in hexane afforded 15.6 mg of 3,4-diphenyl-4-pentenoic acid, mp $161.5\text{--}162.5^\circ$, 38.1 mg of methyl 3,4-diphenyl-4-pentenoate, identical with the compounds previously obtained, and 36.1 mg of 4,4-diphenylcyclopentenone, mp $62\text{--}63^\circ$.

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Stereochemistry at the Methane Carbon in the Di- π -methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry^{1,2}

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Abstract: 3-Ethyl-3,5-dimethyl-1,1-diphenyl-1,4-hexadiene was shown to undergo the di- π -methane rearrangement. Both *cis* and *trans* stereoisomers of 3-ethyl-3-methyl-2-(2'-methylpropenyl)-1,1-diphenylcyclopropane were obtained as photoproducts. This system was used to investigate the stereochemistry of the di- π -methane rearrangement, since the methane carbon is asymmetric. The starting 1,4 diene was synthesized optically active. Also both *cis*- and *trans*-vinylcyclopropane photoproducts were independently synthesized optically active. Then a synthetic route was devised wherein both vinylcyclopropanes and the 1,4 diene were configurationally interrelated. Negatively rotating (365 nm) diene was shown to have the same methane carbon configuration as negatively rotating *cis*-vinylcyclopropane and positively rotating *trans*-vinylcyclopropane. ORD was used throughout to ensure that rotations had no contribution from impurities. After photolysis of the methylethyl diene *cis*- and *trans*-vinylcyclopropanes were separated using recycling high-pressure liquid chromatography and the rotations determined. It was found that in both cases the di- π -methane rearrangement proceeded with inversion of configuration at the methane carbon. The quantum yield for total vinylcyclopropane formation was determined as 0.11. Finally the overall stereochemistry of the di- π -methane rearrangement is discussed.

In our investigations on the di- π -methane rearrangement³⁻¹³ we have elucidated the reaction stereo-

chemistry at two of the three centers of interest. Thus we showed that the stereochemistry at both C-1 and at

(1) This is Paper LXXXVIII on Mechanistic and Exploratory Organic Photochemistry. For the previous paper of the series see ref 2.

(2) (a) For a preliminary communication describing a portion of the present results, see H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *J. Amer. Chem. Soc.*, **96**, 1974 (1974). (b) For the last paper of the series note: H. E. Zimmerman and R. D.

Little, *J. Amer. Chem.* **96**, 4623 (1974).

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