uble rhodium cluster as $Rh_6(CO)_8(PH_3)_8$ is based on compositional analysis and analogy to the known polynuclear $Rh_6(CO)_{16}$ molecule. Molecular weight studies indicate that the palladium and platinum clusters are tetramers and trimers, respectively. A possible structure for the deep red, diamagnetic palladium cluster is a tetrahedron of palladium atoms with the tetrahedral faces bridged by chlorine atoms and with triphenylphosphine and phosphine terminally bonded to palladium. The platinum core cluster may be analogous to $(C_8H_{12})_3Pt_3(SnCl_3)_2$[12] with a triangular array of platinum atoms bridged by iodine atoms above and below the plane. In the rhodium complex $[(C_6H_5)_3P]_2Rh(PH_3)Cl$, obtained in near-colorless needles, there are rather curious infrared characteristics. There is a band at 2350 cm^{-1} which must be assigned to a P–H stretching frequency as well as a very sharp band at 2150 cm^{-1} which must be due primarily to a Rh–H vibration. The molecularity of this particular species has not been determined, but the presence of the band at 2150 cm^{-1} connotes interaction between one of the ligand–hydrogen atoms and the metal atom or that hydrogen abstraction has occurred to give a rhodium(III) species.

A comprehensive account of this new area of chemistry as well as structural details will be published shortly.

(12) L. J. Guggenberger, *Chem. Commun.*, in press.

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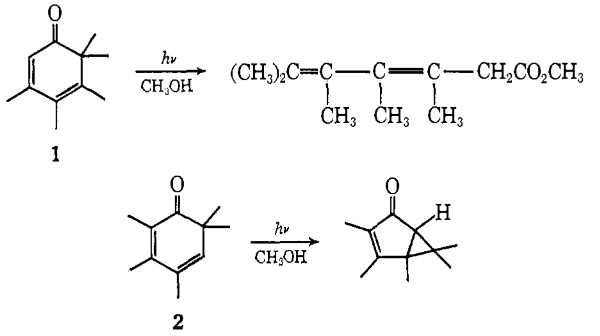
On the Mechanism of 2,4-Cyclohexadienone Photoisomerization

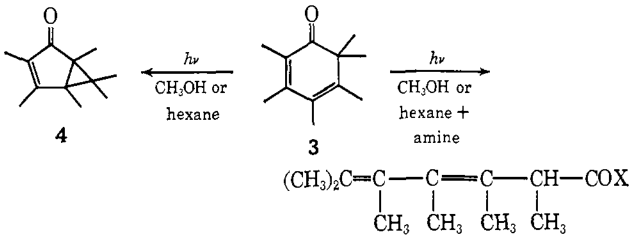
Sir:

Most 2,4-cyclohexadienones undergo reversible ring fission on irradiation to form ketenes which may be trapped by suitable nucleophiles.[1,2,2a] On the other hand certain alkyl-substituted dienones undergo specific photoisomerization to bicyclo[3.1.0]hexenones to the complete exclusion of ring-opened products, even with alcohols as solvent.[3] An important controlling factor in these processes is the pattern of substitution in the dienone, and it has been shown that relatively subtle structural changes have a pronounced effect in determining which of these two reactions is observed.[4] For example, the pentamethyldienones **1** and **2** give only the products shown on irradiation under identical conditions.[4]



In this communication we wish to present evidence that, *in all these cases, the only photochemical reaction is ring opening to a ketene; all other processes, including isomerization to a bicyclo*[*3.1.0*]*hexenone, are thermal.*

Irradiation of dienone **3** in alcohol or hexane gives only ketone **4**. We have now observed that incorporation of dimethylamine in the solvent leads to the photochemical formation of amide **5a** in high yield (92% in hexane).[5] Similar irradiation of **3** in hexane containing cyclohexylamine gave (93% yield) crystalline amide **5b**, mp 80–80.5°.[6]



5a, X = $N(CH_3)_2$
b, X = NH-cyclohexyl

The possibility that a ketene might be a common intermediate in both reactions was confirmed by low-temperature studies. A solution of **3** in methyltetrahydrofuran was irradiated at −100° in a sodium chloride cavity cell, and the course of the reaction was followed by ir spectroscopy. After 20-min exposure the dienone maxima at 1570, 1630, and 1640 cm^{-1} were completely replaced by a single intense absorption at 2100 cm^{-1}, attributable to ketene **6**. When the solution was warmed to room temperature, the ketene absorption band disappeared and was replaced by the original dienone maxima plus a weak band at 1685 cm^{-1} due to a small amount of the ketone **4**. When ethanol was injected into a similar ketene solution at −100° the maxima at 2100 cm^{-1} immediately disappeared, and intense bands due to ketone **4** appeared, together with bands due to a smaller amount of dienone **3**. Thus the ketene may cyclize thermally to either the starting material or to the ketone **4**; indeed, the ketene could not be induced to form **4** photochemically. Cyclization to **4** is favored by the presence of ethanol which, notably, does not react with the ketene to give ester.

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(1) (a) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960); (b) for a review, see G. Quinkert, *Angew. Chem. Intern. Ed. Engl.*, **4**, 211 (1965); (c) P. M. Collins and H. Hart, *J. Chem. Soc., C*, 1197 (1967).

(2) A ketene intermediate has been detected by ir spectroscopy at low temperatures (G. Quinkert, private communication).

(2a) NOTE ADDED IN PROOF. After this paper was submitted, ketene detection was also reported by O. L. Chapman and J. D. Lassila, *J. Am. Chem. Soc.*, **90**, 2449 (1968).

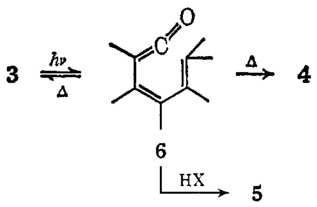
(3) H. Hart, P. M. Collins, and A. J. Waring, *ibid.*, **88**, 1005 (1966).

(4) P. M. Collins and H. Hart, *J. Chem. Soc., C*, 895 (1967).

(5) The structure was deduced from elemental analysis and spectra. Consideration of the nmr spectrum of the amide derived from 3-4-CD_3 eliminated alternative structures which might have arisen from 1,4 or 1,6 addition of amine to the intermediate ketene.

(6) This amide seems to be a single isomer, whereas amide **5a** was a mixture of geometric isomers. The reason for this difference remains to be elucidated.

The simplest scheme that accounts for these observations is shown in eq 1.



(1)

Competition between the three possible reaction pathways was illustrated by an experiment in which various additives were mixed with identical solutions of the ketene at −125°, and the products were analyzed quantitatively after allowing the solutions to attain room temperature. These results are summarized in Table I. Clearly ethanol is superior to methyltetrahydrofuran as a solvent for the formation of ketone **4**, and the effectiveness of an amine to compete with this reaction depends on its nucleophilicity, and possibly its steric requirements.

Table I. The Effect of Ethanol and Amines on the Thermal Reactions of Ketene **6**[a]

Additive	% dienone **3**	% ketone **4**	% amide **5**
None[b]	95	5	
25% ethanol[c]	60	40	
25% ethanol + 1.25×10^{-4} mol of $(CH_3)_2NH$	2	4	94
25% ethanol + 1.25×10^{-4} mol of cyclohexylamine	15	13	72
25% ethanol + 1.25×10^{-4} mol of Et_2NH	43	37	20
1.25×10^{-4} mol of $(CH_3)_2NH$	3	3	94

[a] Ketene was produced by irradiating 10^{-4} mol of **3** in 3 ml of methyltetrahydrofuran through Pyrex at −125°. Additives were introduced at the same temperature, and the mixture was then allowed to slowly warm to room temperature. Products were analyzed by vpc. [b] Overirradiation of the ketene for 2 hr gave no change in yield or product distribution. [c] Irradiation at −125° with the ethanol present from the start gave the same product distribution.

In the range 320–390 mμ, the quantum yield of dienone disappearance or product appearance in ethanol at 25° was 0.46, both in the absence and presence of dimethylamine. The product ranged from only **4** through mixtures to only **5a**, the amount of the latter depending on dimethylamine concentration. Assuming that dimethylamine completely suppresses ketene recyclization to starting dienone (see Table I), the quantum yield for ketene formation must approximate 0.46. This implies that, *in the absence of amine, ketene cyclizes to* **4** *with virtually 100% efficiency in ethanol.*

In amine-free solutions, the quantum yield for appearance of **4** (and disappearance of **3**) decreases with decreasing solvent polarity: 0.46 (methanol), 0.31 (acetonitrile), 0.09 (ether), 0.06 (hexane). In hexane, with dimethylamine present in sufficient amount such that all the product is **5a**, the quantum yield is 0.18. Thus both the quantum yield of ketene formation and the relative rates of its thermal cyclization to **3** or **4** are solvent dependent.

The quantum yield in ethanol with or without amine remains unaltered at 0.46 in the presence of 2 *M* piperylene. Moreover, in the presence of benzophenone or acetophenone the quantum yield decreases markedly when sensitizer absorbs most of the incident light. These results suggest that ketene is formed from a singlet excited state.[7,8]

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(7) The n–π* and π–π* bands in **3** overlap considerably, and a clear decision as to which excited singlet state is involved is not yet possible. An understanding of the structural features which influence the partition of ketene among the three thermal paths awaits further investigation.

(8) We are indebted to a grant from the National Science Foundation for support of this research.