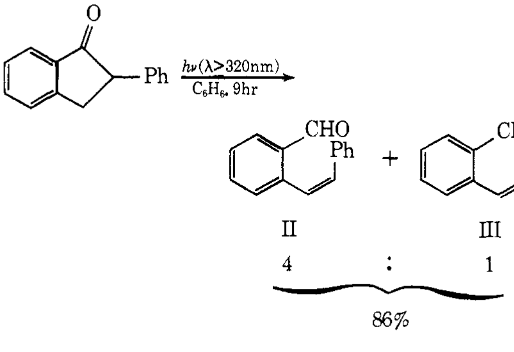
The Photochemistry of 2-Phenyl- and 2,6-Diphenyl-1-indanone

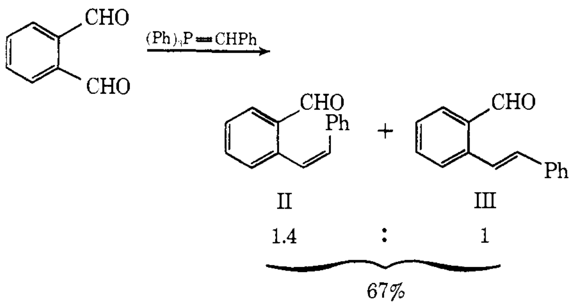
Sir:

The photochemical formation of ketenes and unsaturated aldehydes from cyclopentanones and cyclohexanones has been studied in considerable detail.[1] The reaction has been shown to proceed *via* Norrish type I cleavage of the excited cycloalkanone followed by internal disproportionation of the resulting biradical.[2–4] Triplet (but not singlet) lifetimes decrease with decreasing carbonyl–α-carbon bond energy showing that the triplet state is the reactive one.[5,6] Rates of α cleavage from the triplet have been estimated to be some two orders of magnitude greater than from the excited singlet illustrating a remarkable influence of multiplicity upon reactivity.[5] We wish to report an example of this reaction in a cyclic phenyl ketone, and to present evidence that excited state electronic configuration may also be important in determining the facility of the type I process.

Irradiation (9 hr) of 250 ml of a nitrogen-purged 0.014 *M* benzene solution of 2-phenyl-1-indanone (I)[7] through a uranium-glass filter (λ >3200 Å) with a 450-W medium-pressure mercury lamp resulted in the formation of a 4:1 mixture of two products, II and III, as judged by glpc and nmr analysis. Chromatography of the resulting photolysate on silica gel afforded 0.494 g (86%) of the mixture of products and 0.163 g of unchanged 2-phenylindanone. Rechromatography of the product mixture gave each component in pure form for spectral analysis. The mass spectrum of II and III showed that each was an isomer of the starting material, and nmr, ir, and uv analysis suggested the *cis*- and *trans*-2-stilbenecarboxyaldehyde structures shown in eq 1.[8,9] These structural assignments were confirmed by comparison with authentic samples prepared by the addition of a solution of benzylidenetriphenylphosphorane to a fivefold excess of *o*-phthalic dicarboxaldehyde as shown in eq 2.[10] The formation of 2-stilbenecarboxaldehyde from I could be sensitized by acetophenone and quenched by *cis*-piperylene indicating that in all likelihood the direct photolysis is a triplet reaction. When 0.01 *M* benzene solutions of either 1-indanone or 2-methyl-1-indanone[11] were irradiated as above, only unchanged starting material could be recovered (>90%).



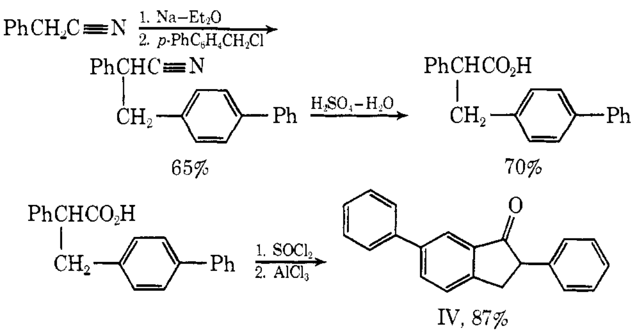
(1)



(2)

Having established the reactivity of 2-phenyl-1-indanone, it was of interest to determine the effect of excited state configuration on the reaction. For this purpose, 2,6-diphenyl-1-indanone (IV) was prepared according to the sequence shown in Scheme I.[9] The expectation that this compound would have a lowest π,π^* triplet state was confirmed by inspection of the phosphorescence spectrum measured at 77°K in EPA, and comparison with that of 2-phenyl-1-indanone (I) (Figures 1 and 2). The phosphorescence from the latter compound showed the expected mirror relationship to the lowest energy (n,π^*) absorption band (E_T = 74 kcal mol^{-1}, ΔE_{S-T} = 4 kcal mol^{-1}), a typical C=O vibronic progression (ν = 1700 cm^{-1}), and a lifetime of 1 msec. However, phosphorescence from the diphenyl derivative IV exhibited a large Stokes shift relative to absorption (E_T = 66 kcal mol^{-1}, ΔE_{S-T} = 12 kcal mol^{-1}), a vibronic progression with $\nu \approx$ 1200 cm^{-1}, and a lifetime of 5.5 sec. These observations indicate that while the lowest energy triplet of I is n,π^*, that of IV has a π,π^* configuration.[12] Additionally, triplet counting experiments in which IV was used as a sensitizer for the

Scheme I. Synthesis of 2,6-Diphenyl-1-indanone



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[1] For a general review see N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, **5**, 92 (1972), and references cited therein.

[2] C. C. Badcock, M. J. Perone, G. O. Pritchard, and B. Rickborn, *J. Amer. Chem. Soc.*, **91**, 543 (1969).

[3] P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969).

[4] A. A. Baum, *Tetrahedron Lett.*, 1817 (1972).

[5] J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2564 (1970).

[6] Yang has reported examples in which both singlet and triplet states of cycloalkanones undergo α cleavage: N. C. Yang and R. H-K. Chen, *ibid.*, **93**, 530 (1971).

[7] Prepared by the method of H. Campbell and E. Ciganek, *J. Chem. Soc.*, 3834 (1956).

[8] Stereochemistry about the double bond was assigned on the basis of vinyl nmr coupling constants—9 Hz for II and 17 Hz for III—and ir absorption at 965 cm^{-1} in III which was absent in II.

[9] Complete spectral data will be presented in our full paper. Satisfactory elemental analyses were obtained for all new compounds.

[10] An incompletely characterized material purported to be 2-stilbenecarboxaldehyde has been prepared from 2-stilbenecarboxylic acid by the method of MacFeyden and Stevens: S. Natelson and S. P. Gottfried, *J. Amer. Chem. Soc.*, **63**, 487 (1941).

[11] Prepared according to the method of W. H. Urry, D. J. Trecker, and H. D. Hartzler, *J. Org. Chem.*, **29**, 1663 (1964).

[12] (a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, Chapters 4 and 5; (b) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

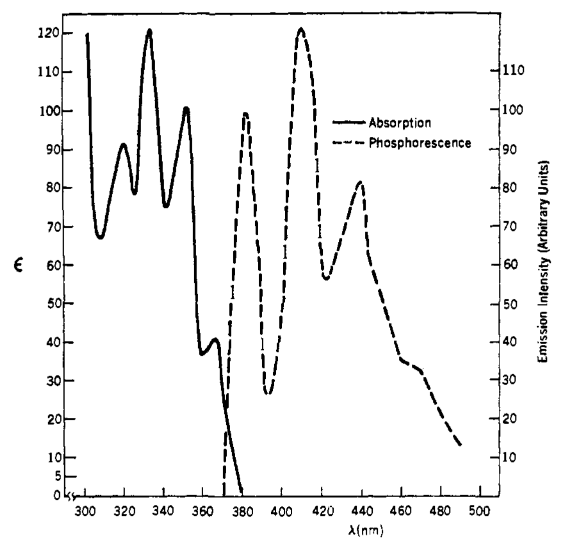

Figure 1. Absorption spectrum (methylcyclohexane) and phosphorescence spectrum (EPA) of 2-phenyl-1-indanone (I).

trans → cis isomerization of stilbene (using 3660 Å light and 0.01 *M* stilbene) showed that intersystem crossing in this ketone occurs with unit efficiency.

Irradiation of a 0.014 *M* benzene solution of IV through a uranium-glass filter for 9 hr resulted in formation of only trace amounts (<5%) of aldehydic material as shown by nmr analysis. Moreover, silica gel chromatography of the crude photolysate afforded 91% recovery of unchanged starting material.

The reactivity of I and the lack of it in IV can be rationalized in terms of localization (or delocalization) of electronic excitation energy. The phosphorescence spectrum of I (Figure 1) clearly shows that (n,π^*) triplet excitation is mainly associated with the carbonyl portion of the molecule. The probability that energy will be concentrated in the vibrational mode leading to CO–CHPh bond dissociation is expected to be large on a purely statistical basis. In IV the lowest lying triplet is π,π^*, and electronic excitation is associated with the entire π system. Indeed, the phosphorescence is more biphenyl like than phenone like.[12a] Concentration of the energy in the appropriate CO–CHPh vibration should be less likely, and reaction is not observed. Alternatively, the reactivity differences can be discussed in the qualitative molecular orbital terms originally presented by Zimmerman.[13] Thus, n,π^* excitation weakens the CO–CHPh σ bond due to increased overlap of the latter with the electron-deficient n orbital of oxygen. When the excited state configuration is π,π^*, no such overlap is possible and reaction does not occur.

The above results suggest that a necessary condition for facile α cleavage of electronically excited ketones is that the lowest energy excited state configuration be n,π^*.[13a] A similar conclusion has been reached regarding the ability of excited ketones to dehydrogenate suitable hydrogen atom donors.[12b] On the other hand, possession of a lowest energy n,π^* triplet is not a *sufficient* condition for cleavage to unsaturated aldehydes in the indanone series. Thus, both 1-indanone and 2-methyl-1-indanone are photostable in benzene solution even though the lowest triplets are n,π^*.[14] Clearly, other factors such as relative values of the excitation energies and bond dissociation energies and excited state geometry play a role in determining reactivity.[15] A complete investigation of the factors influencing reactivity in the cyclic phenyl ketones is currently in progess.

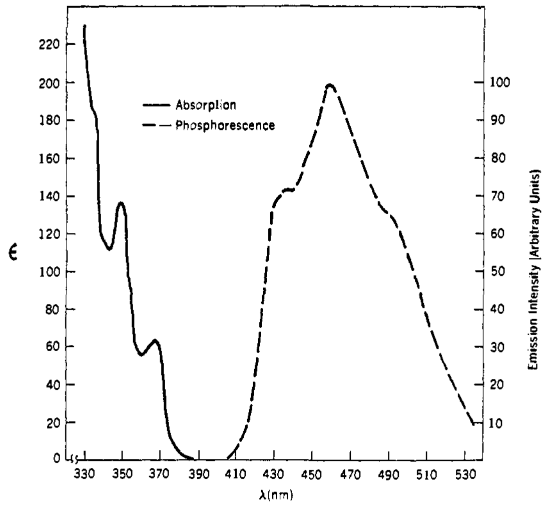

Figure 2. Absorption spectrum (methylcyclohexane) and phosphorescence spectrum (EPA) of 2,6-diphenyl-1-indanone (IV).

Acknowledgment. A helpful discussion with Professor N. C. Yang is gratefully acknowledged.

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(13) H. E. Zimmerman, *Advan. Photochem.*, **1**, 198 (1963).

(13a) NOTE ADDED IN PROOF. After this work was submitted for publication, Lewis reported results which also support this conclusion: F. D. Lewis and J. G. Magyar, *J. Org. Chem.*, **37**, 2102 (1972).

(14) N. Y. C. Chu and D. R. Kearns, *J. Amer. Chem. Soc.*, **94**, 2619 (1972), and references therein.

(15) The CO–CHPh bond dissociation energy in I and IV is estimated to be ~64 kcal mol^{-1}.[16] Thus, the energy content of triplet IV is sufficient to allow for α cleavage.

(16) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

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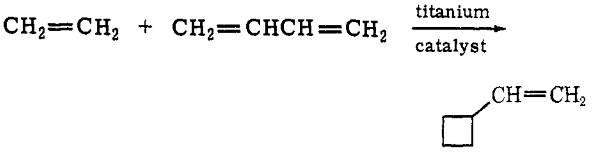
The Cyclodimerization of Ethylene and 1,3-Butadiene to Vinylcyclobutane. Homogeneous Titanium Catalysts

Sir:

The catalyzed cyclodimerization of ethylene and 1,3-butadiene to vinylcyclobutane is here reported for the first time. This is also the first reported instance in



$$CH_2{=}CH_2 + CH_2{=}CHCH{=}CH_2 \xrightarrow[\text{catalyst}]{\text{titanium}}$$

(1)

which ethylene has been involved in a catalyzed reaction giving a four-membered ring.[1] Homogeneous titanium catalysts facilitate vinylcyclobutane production in competition with 1,4-hexadiene, the usual product of

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(1) The cyclotrimerization of butadiene with ethylene to 1,5-cyclodecadiene is known with nickel(0) catalysts; P. Heimbach, P. W. Jolly, and G. Wilke, *Advan. Organometal. Chem.*, **8**, 29 (1970).