with 0.05 and 0.5 M 1,3-cyclohexadiene, respectively. These values, which represent averages of at least two determinations (estimated error ±10%), are in reasonable accord with the efficiencies of benzophenone-sensitized cyclohexadiene dimerization as a function of cyclohexadiene concentration reported by Vesley.[36]

Sensitization Studies. Samples were prepared, irradiated, and analyzed (by glc) in the same way as for quantum yield determinations except that various sensitizers (benzophenone, *m*-methoxy-, and *p*-methoxyacetophenone) were added to the solutions. In each case, the product ratios did not vary significantly from the values obtained on direct irradiation and recorded in Table I.

Spectra. Phosphorescence spectra of keto ester Ia were taken in isopentane and ether–isopentane–ethanol (EPA) glasses at 77°K using an Aminco-Bowman spectrofluorimeter with a phosphorescence attachment.

Acknowledgment. We wish to thank Dr. Ted Evans for the phosphorescence spectra and helpful discussion.

[36] G. F. Vesley, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1968.

Excited-State Three-Ring Bond Opening in Cyclopropyl Ketones. Mechanistic Organic Photochemistry. LX[1]

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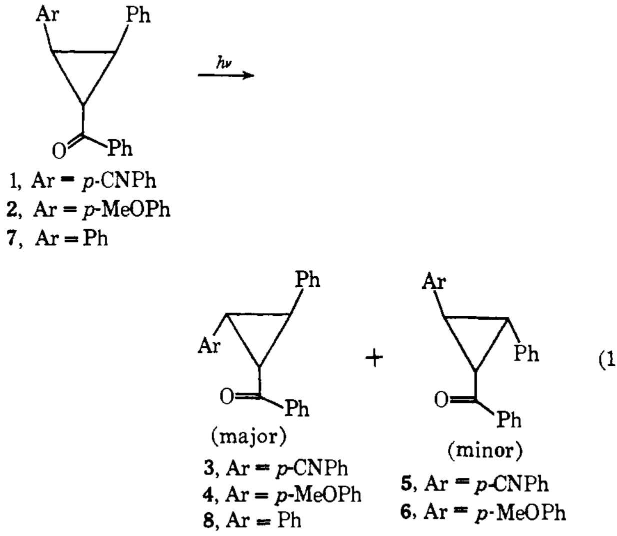
Abstract: The photochemistry of *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane was investigated for comparison with our previous studies on *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane and *trans*-2-*p*-methoxyphenyl-*trans*-3-phenyl-1-benzoylcyclopropane. On both sensitized and direct irradiation a facile stereoisomerization process to yield *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane was observed. The quantum yield for the direct irradiation was 0.94 and that for the acetophenone sensitized reaction was 1.02. Evidence was obtained that the direct irradiation reaction derived primarily from the triplet excited state. Quenching studies allowed estimation of the rate of triplet ring fission and *trans–trans* to *cis–trans* stereoisomerization as $k_r = 3.0 \times 10^{10}$ sec^{-1}. This proves to be very similar to the rate for *trans*-2-*p*-methoxyphenyl-*trans*-3-phenyl-1-benzoylcyclopropane but considerably lower than the rate for *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane. Hence the conclusion may be drawn that despite *p*-methoxyphenyl facilitating three-ring fission, the energetic stabilization is minor, while that deriving from *p*-cyanophenyl is considerable. Surprisingly, despite the isoenergetic nature of the triplet sensitization, energy transfer proved to be of unit efficiency. Isoenergetic transfer is discussed as a phenomenon and one new hypothesis is discussed.

In our recent investigations of excited state electron distribution in cyclopropyl ketones, we utilized *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane[2] (**1**) and *trans*-2-*p*-methoxyphenyl-*trans*-3-phenyl-1-benzoylcyclopropane[3] (**2**). In both of these cases, the reactions observed were stereoisomerizations (note eq 1). These studies afforded both relative rates of different bond fission processes as well as absolute rates of triplet excited state ring opening. For an independent assessment of the energetic importance of the different *para* substituents, it was necessary to ascertain the efficiency and rate of ring fission in the parent molecule lacking the *para* substituents. Thus a study of the photochemistry of *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane (**7**) was initiated.



1, Ar = *p*-CNPh
2, Ar = *p*-MeOPh
7, Ar = Ph

(major)
3, Ar = *p*-CNPh
4, Ar = *p*-MeOPh
8, Ar = Ph

(minor)
5, Ar = *p*-CNPh
6, Ar = *p*-MeOPh

(1)

Results

Reaction Product, Quantum Yield, Sensitization, and Quenching Studies. Exploratory studies of the irradiation of *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane (**7**) revealed a particularly clean conversion to the *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane stereoisomer (**8**). The structure of this stereoisomer was established firmly by independent synthesis as detailed in the Experimental Section.

Our study began with investigation of the reaction efficiency. Irradiation in benzene at 313 nm in our "black box" apparatus[4] and ferrioxalate actinometry[5]

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* Address correspondence to this author.

[1] For paper LIX see H. E. Zimmerman and V. J. Hull, *J. Amer. Chem. Soc.*, in press.

[2] H. E. Zimmerman, S. S. Hixson, and E. F. McBride, *ibid.*, **92**, 2000 (1970).

[3] H. E. Zimmerman and C. M. Moore, *ibid.*, **92**, 2023 (1970).

[4] (a) Described as apparatus B by H. E. Zimmerman, H. G. Dürr, R. S. Givens, and R. G. Lewis, *ibid.*, **89**, 1863 (1967). (b) The apparent quantum yield decreased with time due to light absorption by-product and very minor but strongly absorbing impurities.

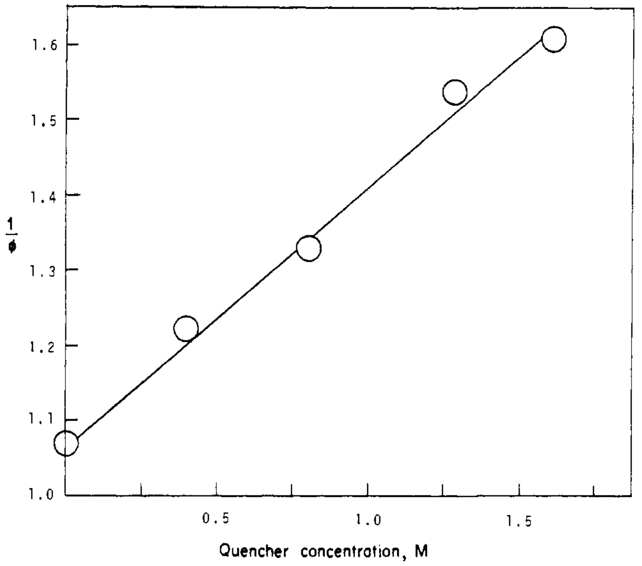


Figure 1. Stern–Volmer plot of quenching of *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane with piperylene.

revealed a particularly facile reaction with a quantum yield of $\Phi = 0.94$ at low conversion. Acetophenone sensitization, with the sensitizer capturing greater than 99% of the light, gave an efficiency of $\Phi = 1.02$. The direct and sensitized runs are summarized in Table I.

Table I. Quantum Yields of Direct and Acetophenone-Sensitized Irradiations of *trans,trans*-2,3-Diphenyl-1-benzoylcyclopropane

Run[a,b]	Acetophenone concn, *M*[c]	Conversion, %	Quantum yield, **8**
1		4.9	0.94
2		8.7	0.72
3		33.0	0.39
4	0.94	14.0	1.02
5	0.94	17.5	0.90

[a] All runs were made with filter transmitting 300–330 nm. [b] Benzene solvent. [c] Over 99% light capture by acetophenone.

In order to obtain information required for the determination of the rate of reaction of the triplet excited state, quenching studies using piperylene were initiated. These results are listed in Table II. It is seen that quenching by piperylene was effective and with 1.6 *M* piperylene the reaction could be quenched to the extent of 35%. Under the conditions of these runs, light capture by quencher and any potential impurities developing during the reaction could be shown to be less than 2%.

Table II. Piperylene-Quenched Irradiations of *trans,trans*-2,3-Diphenyl-1-benzoylcyclopropane

Run[a–c]	Piperylene concn, *M*	Conversion, %	Quantum yield, **8**
1	0.40	3.9	0.82
2	0.80	3.3	0.75
3	1.30	3.0	0.65
4	1.60	3.8	0.62

[a] All runs were with filter transmitting 300–330 nm. [b] Benzene solvent. [c] Over 98% light capture by reactant.

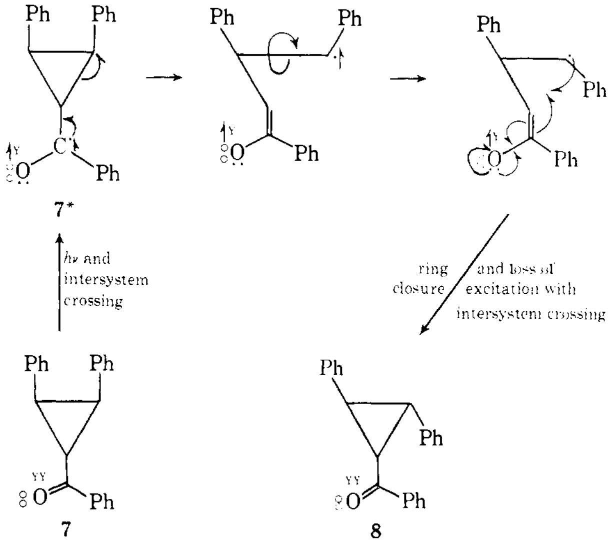
A Stern–Volmer plot of the reciprocal of the quantum yield *vs.* quencher concentration is given in Figure 1. Fitted to eq 2, the slope was calculated to be 0.34 and the intercept to be 1.07.

$$\frac{1}{\Phi} = \frac{k_r + k_d}{k_r} + \frac{k_q[Q]}{k_r} \tag{2}$$

In order to assess the relative energies of the triplets involved in the sensitized irradiations, the phosphoresence emission spectrum of *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane (**7**) in 75:19 methylcyclohexane–isopentane glass at 77°K was determined. The 0–0 band appeared at 384.4 nm and the entire spectrum displayed vibrational structure with a spacing of 1700 cm^{-1}. This compares well with the stretching frequency of 1690 cm^{-1} found in the infrared spectrum of **7**. Finally, the zero-point energy is thus seen to be 74.2 kcal/mol.

Interpretive Discussion. Efficiency, Sensitization, and Quenching Data. The finding of a 0.94 direct irradiation quantum yield adds the present stereoisomerization of *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane (**7**) to *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane (**8**) to the relatively small list of essentially perfectly efficient photochemical reactions. The high efficiency of the stereoisomerization is reasonable if one contemplates the three-ring strain dissipated by bond opening of the excited state as shown in the mechanism in Chart I.

Chart I. The Mechanism of the Conversion of *trans,trans*-2,3-Diphenyl-1-benzoylcyclopropane (**7**) to *cis,trans*-2,3-Diphenyl-1-benzoylcyclopropane (**8**)



That acetophenone sensitization gives the same efficiency, within experimental error, in an experiment in which the triplet is artificially engendered, is highly suggestive that the triplet is also the reacting species in the direct irradiation. At a minimum this shows that the triplet rearranges successfully and with unit efficiency.

One further interesting aspect of the sensitization experiment is its high efficiency despite the isoenergetic nature of the transfer. Thus acetophenone is known[6] to have a triplet energy of 73.6 kcal/mol and *trans,*-*trans*-2,3-diphenyl-1-benzoylcyclopropane was found

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(5) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(6) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(*vide supra*) to have a triplet energy of 74.2 kcal/mol. One might have anticipated that without an appreciably exothermic transfer of at least 3 kcal/mol,[7] from sensitizer to reactant, a less than perfectly efficient process would ensue.

One rationale which is particularly intriguing is that once there is an encounter between sensitizer and reactant, the probability of transfer may be enhanced by the availability of an exceedingly rapid molecular transformation by the excited state of reactant. The availability of such a molecular transformation will influence the efficiency of triplet transfer because the overall rate of transfer is the product of the rate of diffusion (*i.e.*, encounter rate) and the probability of energy transfer following diffusion together. For an isoenergetic transfer there will be many collisions in the solvent cage during each encounter[8] with reversible exchange of the excitation energy; here the rate of the excited-state reaction may be of the same order of magnitude as the rate of diffusion apart of the two species, donor and reactant. If so, the probability of successful energy transfer will depend on the excited state reaction rate and a rapid reaction willl have a better chance to occur than a slow one. Accordingly, the intriguing possibility suggests itself that for isoenergetic sensitization the effectiveness of transfer will in general be controlled by the energy barrier for the reaction of the energy acceptor.

In the photochemistry at hand, this would mean that a sensitizer–reactant pair in a solvent cage is very unlikely to diffuse apart without energy transfer because the three-ring opening is very rapid and will compete with such diffusion.

A second rationale is that a single isoenergetic collision might conceivably be perfectly efficient in energy transfer if the subsequent reaction occurs concertedly with the energy-transfer process. This has been termed nonvertical excitation by Hammond.[9,10]

It was noted above that the sensitization results suggested but did not prove that a triplet was the reacting species in the direct irradiations. However, the quenching studies, in which up to 35% of the reaction was quenched by piperylene, indicate that at least a very appreciable fraction of the reaction proceeds by a triplet. The concentrations used were in the range where singlet transfer would not be expected.[11] This point is considered again in light of the quenching results (*vide infra*).

Stern–Volmer treatment of the quenching data allowed determination of the rate of the excited state reacting as $k_r = 3.0 \times 10^{10}$ sec^{-1}. This assumes a rate of diffusion in benzene[12] of 1×10^{10} l. mol^{-1} sec^{-1}. The decay rate obtained from the same treatment was $k_d = 2.1 \times 10^9$ sec^{-1}.[14]

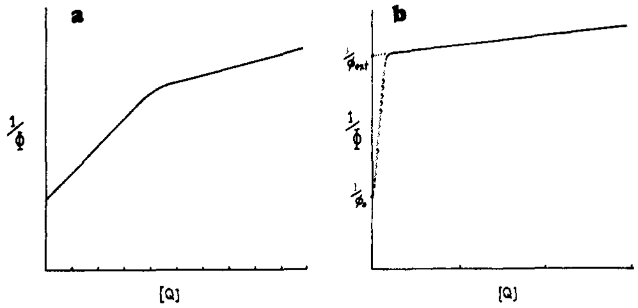

Figure 2. Stern–Volmer plots involving two multiplicity species, shown over broad and only high quencher concentration ranges.

As noted above, one might concern himself with the possibility that it is instead S_1, or perhaps both S_1 and T_1, which is being quenched.[15] However, the Stern–Volmer treatment (*vide supra*) allows a firm conclusion that a single excited state is indeed being quenched and that this excited state is T_1, the lowest triplet. The approach is generally applicable and operates as follows.

Where two multiplicity excited states, T_1 and S_1, are quenched in a reaction, one finds that there are *two* linear regions of the plot, as in Figure 2a. The first and steep portion represents primarily quenching of the longer lived triplet and the lower sloped portion results from less efficient singlet quenching. This clearly is not the case presently. But one might worry that, with the relatively high piperylene concentrations used, the steep portion of the curve might be missed in the plot as shown in Figure 2b. This could be mistaken for quenching of a singlet excited state. However, if this were the case, the intercept, *i.e.*, $(1/\Phi)_{\mathrm{extr}}$, should be larger than and different from the reciprocal of the unquenched quantum yield, *i.e.*, $(1/\Phi_0)$. Presently, we find, however, that $(1/\Phi)_{\mathrm{extr}} = 1.03$ and $(1/\Phi_0) = 1.07$. In the event of an appreciable portion of nonquenchable singlet component, one would not obtain a linear Stern–Volmer plot. Thus we must conclude that, within experimental error, a single excited state is involved.

Then we note that $k_d = 2.1 \times 10^9$ sec^{-1}. This is too slow a decay to allow this excited state to be a singlet, since benzoyl singlets are known[13] to decay by intersystem crossing at a rate of over 10^{10} sec^{-1}. The evidence therefore excludes S_1 and leaves us with T_1. Thus the reaction efficiency is that found independently for T_1 and the reaction is known to derive minimally 35% from T_1.

The triplet reaction rate may now be compared with that for the related *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**1**).[2] The rate is seen to be tenfold slower than that for **1** but quite similar to the 1.5

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[7] (a) G. Porter and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **264**, 1 (1961). (b) It is known that diffusion control is reached asymptotically over a *ca.* 10 kcal/mol exothermicity range with efficiency of transfer being only *ca.* one-fourth diffusion controlled at 7 kcal/mol (H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, **90**, 3749 (1968)).

[8] K. J. Laidler, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1956, p 202.

[9] G. S. Hammond and J. Saltiel, *J. Amer. Chem. Soc.*, **85**, 2515, 2516 (1963).

[10] S. L. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, **90**, 2957 (1968).

[11] Thus, with a bimolecular rate of diffusion of 1×10^{10} l. mol^{-1} sec^{-1} in benzene[12] and a quencher concentration of, *e.g.*, 0.5 *M*, the rate of collision becomes 5×10^9 sec^{-1} which is too slow to allow collisions of excited singlets with quencher to compete with the rate of loss of singlets by intersystem crossing. The latter should be[13] greater than 1×10^{10} sec^{-1}.

[12] F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

[13] F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).

[14] That piperylene quenches with an efficiency that is within a order of magnitude of the rate of diffusion is shown in: H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, **90**, 3749 (1968).

[15] Thus, very recently evidence has been presented by F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem.Soc.*, **92**, 1793 (1970), that some singlet excited states are capable of being quenched by piperylene at very high piperylene concentrations (*i.e.*, 1–10 *M*). We note, however, that such quenching is most likely at concentrations higher than the present study and in the case of alkyl ketones where intersystem crossing is slower than presently.

$\times\ 10^{10}$ sec^{-1} rate found for *trans*-2-*p*-methoxyphenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**2**).[3] This suggests that *p*-cyano substitution has substantial effect on the ease of excited-state ring opening but that *p*-methoxy substitution has little effect on this process.

In order to proceed to an interpretation of these effects, one needs to inspect the mechanism proposed for the stereoisomerization process. This is delineated in Chart I. The relative rates are understood if it is recognized that the ring-opening process is facilitated by stabilization of the odd-electron center by *p*-cyanophenyl. This is confirmed by the selectivity observed in our earlier work[2] in which the rate of fission of the three-ring bond between the *p*-cyanophenyl and benzoyl groups was at least ten times the rate of fission of the three-ring phenyl–benzoyl bond. The smaller selectivity observed for the *p*-methoxyphenyl case (4:1)[3] confirms the lesser stabilization due to the methoxy substituent relative to the cyano.[16]

The intermolecular rate comparison reinforces the point that the three-membered ring is definitely not electron deficient in the excited state undergoing ring opening. The observation of the n–π^* triplet in the phosphoresence spectrum makes this species the most reasonable excited state to account for the observed behavior since this species will not be electron deficient in the three ring and also will lead to a species stabilized by an electron-withdrawing substitutent.

Finally, one philosophical point needs explicit commentary. Throughout the present discussion it has been assumed that the course of molecular transformation of an electronically excited species is controlled by energetic factors. We have assumed that an excited-state species will follow those molecular pathways for change which minimize its energy. Such a hypothesis was made by us nearly a decade ago[17] and yet is still controversial. Nevertheless, perusal of the present photochemistry as well as other transformations from the literature does seem to support this hypothesis.

Experimental Section[18]

Solvent Pruification. Benzene used in photolyses was purified by shaking four times with concentrated sulfuric acid, three times with aqueous sodium bicarbonate, drying with sodium sulfate, and distilling from phosphorus pentoxide onto freshly pressed sodium wire.

cis-**Stilbene.** This material was obtained in 65–80% yield by photolysis of the trans isomer in hexane.

α-**Diazoacetophenone.** This materal was prepared by the method of Newman and Beal[19] in 60–80% yield, mp 46–47° (lit.[19] 47.8–48.4°).

trans,trans-**2,3-Diphenyl-1-benzoylcyclopropane.** This material was prepared by the method of Zimmerman and Hixson.[2] A solution of 13.40 g (0.0910 mol) of α-diazoacetophenone in 24 ml of xylene was added dropwise over 2 hr to 8.436 g (0.0486 mol) of *cis*-stilbene in 2.0 ml of xylene containing 1.00 g of copper bronze (Luco No. 16, Leo Uhlfelder Co., New York, N.Y., analyzed for 99.5% copper). The slurry was heated at 132° during the addition of the α-diazoacetophenone and a total of 2640 ml (98% of theoretical) of nitrogen was evolved.

The catalyst was filtered from the cooled, dark brown solution, the solvent removed *in vacuo*, and the residue chromatographed on a 6 × 79 cm silica gel column slurry-packed with 1% ether–hexane. Elution was with 3 l. of 1% ether–hexane, 4 l. of 2%, 2 l. of 5%, 4 l. of 10%, 14 l. of 20%, and 6 l. of 50%; 1-l. fractions were collected. Fractions 10–13 contained 6.697 g of an oil consisting of both *cis*-stilbene and the desired ketone; 14–23, 4.843 g of the desired ketone; and 24–33, 8.702 g of unidentified material. Fractions 10–13 and 14–23 were separately chromatographed on a 6.5 × 28 cm silica gel column prepared and eluted as above. A total of 5.131 g of oil was collected and crystallized from ether–hexane to yield 1.934 g (14% based on reacted *cis*-stilbene) of the ketone, mp 91–91.5° (lit.[20] 90–92°).

The spectral data were: ir ($CHCl_3$) 3.25, 3.31, 6.01, 6.25, 6.33, 6.70, 6.91, 7.08, 7.54, 7.77, 8.48, 9.30, 9.92, 10.03, 11.57, 14.50, 15.20 μ; uv (cyclohexane) 250 nm max (ϵ 20,000), n–π^* sh 320 nm (ϵ 196); nmr ($CDCl_3$) τ 1.84–2.00 (m, 2 H, *o*-benzoyl), 2.45–3.10 (m, 13 H, arom), 6.35–6.76 (m, 3 H, cyclopropyl).

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.58; H, 6.05.

cis,trans-**2,3-Diphenyl-1-benzoylcyclopropane.** This material was prepared by the same method[2] as the *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane. A total of 23.101 g (0.128 mol) of *trans*-stilbene and 21.628 g (0.148 mol) of α-diazoacetophenone were converted to 3.010 g (20% based on reacted stilbene) of *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane, mp 156–157°. The spectral data were: ir ($CHCl_3$) 3.25, 3.32, 5.98, 6.23, 6.32, 6.67, 6.90, 7.32, 7.88, 8.49, 9.77, 10.26, 14.40 μ; uv (cyclohexane) 247 nm max (ϵ 7650), 320 nm max (ϵ 480); nmr ($CDCl_3$) τ 1.97–2.17 (m, 2 H, *o*-benzoyl), 2.40–3.00 (m, 13 H, arom), 6.26–6.79 (m, 3 H, cyclopropyl).

Anal. Calcd for $C_{12}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.72; H, 6.15.

Photolysis Apparatus. The "black box" irradiation apparatus[4] used a General Electric AH6 mercury arc in a deep parabolic reflector. The 12-cm beam was filtered through a 2.0-mm Corex D plate (Corning No. 9700) and through a three-compartment, water-cooled solution filter (*vide infra*). The sample cell was maintained at 25.0 ± 0.2° and deoxygenated nitrogen[21] was bubbled through the photolysis solution.

Filter Solutions. The system used in all irradiations[2] consisted of: cell 1, 0.76 *M* cobalt sulfate and 0.08 *M* cupric sulfate in 10% sulfuric acid; cell 2, 0.89 *M* nickelous sulfate in 10% sulfuric acid; cell 3, 1.29 m*M* potassium chromate and 0.36 *M* potassium carbonate in water. Transmission was 0% below 300 nm, 11% at 313 nm, and 0% above 330 nm.

Actinometry. Incident light was measured by potassium ferrioxalate actinometry[5] before and after the sample run and was monitored for transmission through the sample cell by an actinometer cell behind the sample cell during the sample run. The quantum yield for the ferric ion reduction was taken to be 1.25 for the wavelength used.

Quantum Yield Irradiations. The general procedure was as follows. A sample of *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane was dissolved in purified benzene and freshly purified piperylene or acetophenone (if any) up to a total of 730 ml. The sample solution was deoxygenated by bubbling purified nitrogen[21] through it for 1 hr before photolysis. The actinometry and sample irradiation were then carried out and the solvent stripped from the sample solution *in vacuo*. The residue was chromatographed on a 2 × 116 cm column slurry-packed with Mallinckrodt AR silicic acid in 8% ether–hexane and eluted with the same solvent system. The eluent absorbance as monitored at 280 nm and 20-ml fractions were collected. Two such chromatograms were usually necessary for complete separation of the two isomers. The ir and nmr spectra of the photoproduct and its melting point were exactly the same as those of *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane. A mixture melting point of the photoproduct and the synthetic material was undepressed. The uv spectra of the sample and filter solutions were checked before and after photolysis. No change was observed except for the direct irradiations where absorbance increased with extent of irradiation.

Specific data for individual irradiations are given as follows: weight of *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane, identity of additive (if any), weight of additive, concentration of additive, amount of light absorbed, amount of *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane, quantum yield.

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(16) The uncertainty in measuring the slopes and a lesser error in the measured selectivity accounts for the small discrepancy in the relative rates as otained from inter- *vs.* intramolecular bond-fission competitions.

(17) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **83**, 4486 (1961), and H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962).

(18) Melting points were taken on a hot stage apparatus calibrated with known compounds.

(19) M. Newman and P. Beal, *J. Amer. Chem. Soc.*, **71**, 1506 (1949).

(20) R. Breslow, J. Brown, and J. J. Gajewski, *ibid.*, **89**, 4383 (1967).

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

Run QY-1: 630.0 mg, no additive, 0.111 mEinstein, 31.0 mg of product, 0.94.

Run QY-2: 355.6 mg, no additive, 0.138 mEinstein, 30.9 mg of product, 0.72.

Run QY-3: 299.4 mg, no additive, 0.850 mEinstein, 55.5 mg of product, 0.39.

Run QY-Q1: 646.1 mg, piperylene, 42.5 g, 0.40 *M*, 0.106 mEinstein, 25.1 mg of product, 0.82.

Run QY-Q2: 639.7 mg, piperylene, 85.7 g, 0.80 *M*, 0.106 mEinstein, 21.3 mg of product, 0.75.

Run QY-Q3: 641.0 mg, piperylene, 139.0 g, 1.30 *M*, 0.107 mEinstein, 19.0 mg of product, 0.65.

Run QY-Q4: 560.0 mg, piperylene, 171.2 g, 1.60 *M*, 0.117 mEinstein, 21.6 mg of product, 0.62.

Run QY-S1: 296.0 mg, acetophenone, 82.3 g, 0.94 *M*, 0.141 mEinstein, 43.0 mg of product, 1.02.

Run QY-S2: 298.6 mg, acetophenone, 82.3 g, 0.94 *M*, 0.194 mEinstein, 52.1 mg of product, 0.90.

Phosphorescence Emission Spectrum of *trans,trans*-2,3-Diphenyl-1-benzoylcyclopropane. The emission spectrum of the ketone was determined on an Aminco-Bowman spectrophosphorimeter in 75:19 methylcyclohexane–isopentane glass at liquid nitrogen temperature at a concentration of 10.0 m*M*. The signal was enhanced using the program XY time averager[22] on a PDP-8/I computer.[23] The spectrum consisted of a progression of bands at 384.4, 410.2, 439.8, 472.2, and 506.6 nm.

Acknowledgment. Support of this research by the Army Research Office (Durham) is gratefully acknowledged. T. W. F. expresses appreciation to the National Science Foundation for a Summer Fellowship (1966) and to the National Institutes of Health for a Predoctoral Fellowship (1966–1969).

[22] This program was written in these laboratories. Special thanks are due to R. McKelvey for performing this experiment.

[23] Digital Equipment Corporation, Maynard, Mass.

Introduction of the Amide Function into 1,3,2-Dioxaphospholenes with Pentavalent Phosphorus

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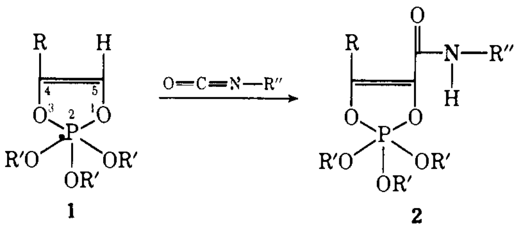
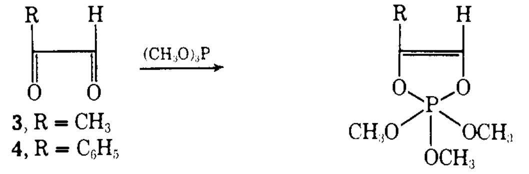
Abstract: Carbamyl-1,3,2-dioxaphospholenes with pentavalent phosphorus were synthesized from α-ketoaldehydes, isocyanates, and trialkyl phosphites. The phospholenes were converted into phosphate esters of β-keto-α-hydroxyamides. These underwent very rapid hydrolyses to β-keto-α-hydroxyamides.

The 2,2,2-trialkoxy-1,3,2-dioxaphospholenes (**1**) are versatile reagents in organic synthesis.[2] They are readily prepared from α-dicarbonyl compounds and trialkyl phosphites.[2] This paper describes a new reaction whose net effect is to replace the hydrogen atom on the phospholene ring by the amide function. The carbamylphospholenes (**2**) are the high-energy orthophosphate esters[3] of the enediol tautomers of β-keto-α-hydroxyamides.



Results

Reaction of Pyruvaldehyde with Trimethyl Phosphite. Aqueous pyruvaldehyde (**3**) was dehydrated and converted into the phospholene **5** by reaction with trimethyl phosphite. Anhydrous pyruvaldehyde was also made, but less conveniently, from dihydroxyacetone[4] and from acetone.[5]



3, R = CH_3
4, R = C_6H_5

5, R = CH_3; $\delta^{31}P = +44.8$ ppm *vs.* H_3PO_4
6, R = C_6H_5; $\delta^{31}P = +45.4$ ppm

The structure of **5** was based on the ^{31}P nmr shift and on the data of Table I. The molecule is assumed to be a trigonal bipyramid in which case it can exist as three diastereomers,[6] all meso forms. The three methoxy groups of **5** gave one ^1H nmr signal at 20°, and the spectrum did not change at −90°. This pentaoxyphosphorane, as its analogs,[2] undergoes rapid positional exchange of groups by pseudorotation[7] or by other mechanisms.[8]

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[2] (a) F. Ramirez, *Accounts Chem. Res.*, 1, 168 (1968); (b) F. Ramirez, *Bull. Soc. Chim. Fr.*, 2443 (1966); (c) F. Ramirez, *Pure Appl. Chem.*, 9, 337 (1964).

[3] The ortho state of phosphoric acid is pentahydroxyphosphorane, $(HO)_5P$, in the sense that orthocarbonic acid is $(HO)_4C$ and orthoformic acid is $(HO)_3CH$.

[4] H. O. L. Fischer and L. Feldmans, *Chem. Ber.*, 62, 864 (1929).

[5] H. L. Riley, J. Morley, and N. A. C. Friend, *J. Chem. Soc.*, 1875 (1932).

[6] There are 20 isomers of P(1, 2, 3, 4, 5) if the five ligands are different but symmetric. Two isomers are excluded in cyclic oxyphosphoranes because the ring cannot be diapical. In the present case, **5**, three ligands are identical, which combined with other symmetry properties of the molecule, results in the three isomers *a*, $\bar{j}$, $\bar{h}$. The remaining bipyramids will be equivalent to these three and simply disclose the positional exchange of the groups.

[7] (a) F. Ramirez, J. F. Pilot, C. P. Smith, S. B. Bhatia, and A. S. Gulati, *J. Org. Chem.*, 34, 3385 (1969); (b) P. C. Lauterbur and F.