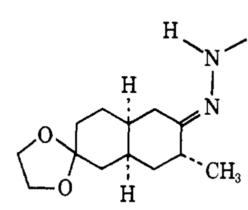
may be carried out in 65% yield without purification of the intermediates.



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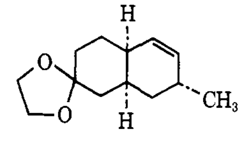

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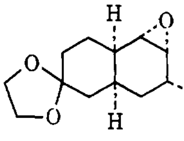

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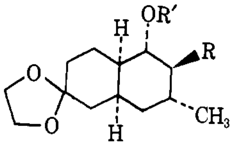
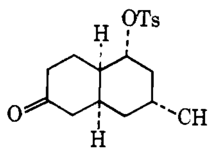


11, $R = SC_6H_5$; $R' = H$
12, $R = H$; $R' = H$
13, $R = H$; $R' = Ts$

Treatment of **12** with *p*-TsCl in pyridine at 50° for 10 hr followed by acid hydrolysis of the ketal tosylate **13** (acetone, HCl, 50° for 45 min) afforded keto tosylate **14**, mp 99–100°, in 89% yield.

Introduction of the *N*-methylamine moiety into the bicyclic ketal tosylate **13** formally constitutes a simple transformation. However, both the sterically congested concave face of the cis decalyl system and the observed tendency of cyclohexyl tosylates to undergo elimination in addition to substitution[9,10] with amine nucleophiles suggested that the elimination pathway would predominate in any attempted direct displacement process on **13**. As anticipated, treatment of **13** with either methylamine or azide ion under a variety of conditions afforded olefin as well as minor amounts of substitution products. In an attempt to circumvent this problem, the ketal function was removed in anticipation that tosylate displacement could be effected by an intra- rather than intermolecular pathway (*cf.* **15**).



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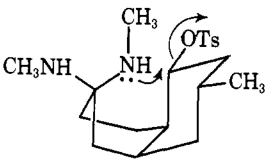

15

Indeed, when **14** was treated with excess monomethylamine in benzene (sealed tube, 75°, 24 hr) the desired ketoamine **2** was obtained in 94% yield uncontaminated by olefin. Although the existence of **15** is only postulated, the facility with which substitution occurs in this system renders intramolecular delivery of nitrogen through aminal **15** a distinct possibility.

With our key intermediate, **2**, now in hand the final step was accomplished by heating **2** with paraformaldehyde in 3-methylbutan-1-ol (reflux, 20 hr) to afford (±)-luciduline (**1**) (mp of HCl salt, 179–181°), identical by ir (liquid film), nmr, mass spectrum, and vpc with an authentic sample of **1**.[11]

Acknowledgment. We are grateful to Professor W. A. Ayer for an authentic sample of luciduline and to the National Institutes of Health for generous support of this research.

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(9) J. L. Pinkus, G. Pinkus, and T. Cohen, *J. Org. Chem.*, 27, 4356 (1962).

(10) (a) A. K. Bose, J. T. Kistner, and L. Farber, *ibid.*, 27, 2925 (1962); (b) E. J. Corey and R. L. Dawson, *J. Amer. Chem. Soc.*, **85**, 1782 (1963).

(11) Satisfactory combustion analyses where obtained on all synthetic intermediates with the exception of **9**.

(12) Camille and Henry Dreyfus Teacher–Scholar Recipient, 1971–1976; Alfred P. Sloan Fellow, 1972–1974.

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Received March 31, 1972

Irradiation of Triaryl Phosphate Esters. A New Photochemical Coupling Reaction[1]

Sir:

While searching for new reactions analogous to those observed when aryl *carboxylate* esters are irradiated,[2] we examined the photochemistry of various *phosphate* esters and discovered a new photochemical coupling process whose novelty and potential utility prompts this preliminary communication. The major characteristic of this new reaction, as illustrated in eq 1, is the

$$(ArO)_3PO \xrightarrow{h\nu} Ar\text{–}Ar + ArOPO_3H_2 \qquad (1)$$

formation of a new carbon–carbon bond between two of the aryl groups in the ester, resulting in the production of a biphenyl derivative along with the corresponding monoaryl phosphate. Some of our results are collected in Table I.

In contrast to the photodecarboxylation reaction of aryl carboxylates,[3] in which the coupling step is accompanied by the expulsion of a stable molecule (eq 2), the

$$RCO_2Ar \xrightarrow{h\nu} RAr + CO_2 \qquad (2)$$
$$R = \text{alkyl or aryl}$$

phosphate coupling reaction (eq 1) involves an oxidation–reduction sequence at some stage. The solvent ethanol most likely serves as reductant and, indeed, we have isolated acetaldehyde as its 2,4-dinitrophenylhydrazone derivative. Another contrasting feature is that neither photo-Fries products (*i.e.*, hydroxyaryl phosphonates) nor solvolysis products (*i.e.*, diaryl ethyl, aryl diethyl, or triethyl phosphate) were detected in any of the experiments listed in Table I.[4]

The lack of, *e.g.*, toluene from tri-*p*-cresyl phosphate, anisole from trianisyl phosphate, etc., or any of the corresponding ethyl ethers, strongly diminishes the possibility that free aryl radicals, carbanions, or carbonium ions are produced during the reaction. When an equimolar mixture of triphenyl and tri-*p*-cresyl phosphates in ethanol solution was irradiated for 4.5 hr, there was obtained only biphenyl (21% yield, 4% conversion) and 4,4′-dimethylbiphenyl (53% yield, 48% conversion) in the biaryl fraction. Likewise, when a similar mixture of tri-*p*-cresyl phosphate and tri-*p*-

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(1) (a) Photochemical Studies. VIII. For part VII in this series, see ref 2. (b) Financial support for this work was generously provided by the National Science Foundation (GP 5785) and the National Institutes of Health (GM 11412).

(2) R. A. Finnegan and D. Knutson, *Tetrahedron Lett.*, 3429 (1968).

(3) Reference 2 and earlier articles in this series cited therein.

(4) Although the corresponding phenols were usually observed, they were shown to arise during the analysis (vpc) by thermal decomposition of the monoaryl phosphate. They could not be isolated by silica gel column chromatography.

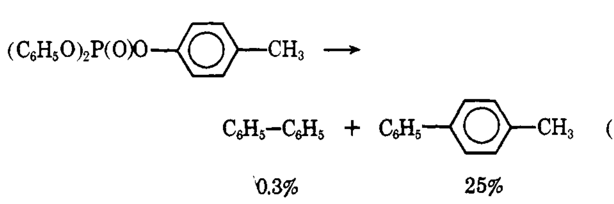
Table I. Irradiation of Symmetrical Triaryl Phosphates, $(ArO)_3PO$[a]

Ar	Ar-Ar % yield	$10^4\Phi$[b]	$ArOPO_3H_2$ % yield	Recovered ester, %
Phenyl	2	6		48
p-t-Butylphenyl	51	44	55	24
p-Tolyl	35-51	190	2-10[c]	13-20
p-Anisyl	81	370	38	17
p-Chlorophenyl	3[d]	*e*		36[d]
Mesityl	4	*e*	7	7

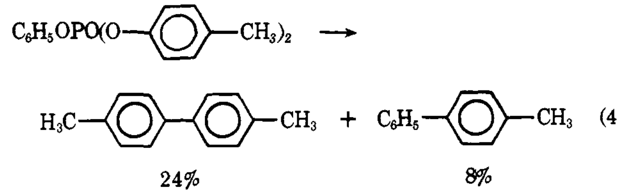
[a] These esters were irradiated as *ca.* 0.02 *M* solutions in ethanol for about 5 hr, using a 450-W Hanovia medium-pressure mercury arc lamp housed in a double-walled quartz immersion well. Solutions were deoxygenated by passing a stream of argon through a sintered disk at the bottom of the reaction vessel for a period of 0.5 hr prior to turning on the lamp, and continuing during the course of the reaction. The temperature of the photolyzing solution was maintained between 35 and 50°. All new materials were characterized by ir, nmr, and microanalysis. Products were identified by direct ir, nmr, vpc, or mixture melting point comparisons with authentic or independently prepared samples. [b] Quantum yields for biaryl formation were determined at 2537 Å by the "merry-go-round" method in a Rayonet photochemical reactor. The lamp intensity ($3.123 \pm 0.518 \times 10^{15}$ quanta/sec) was measured by means of the cyclopentanone actinometer (J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 1318 (1970); P. Dunion and C. N. Trumbore, *ibid.*, **87**, 4211 (1965)). Conversions were held to 7–8% and analyses were carried out by gas chromatography. [c] These low yields are no doubt due to the inefficiency of the isolation technique employed. Recently we have obtained this product in 52% yield when isolated as its biscyclohexylammonium salt. [d] This biaryl is actually a mixture of 4,4′-dichlorobiphenyl, 4-chlorobiphenyl, and biphenyl in the ratio 41:44:15. Similarly, the recovered starting material is actually a mixture of esters containing three, two, one, and zero chlorine atoms, in the ratio 43:32:17:8. This phenomenon of photodehalogenation has been documented by other workers (E. A. Caress and I. E. Rosenberg, *J. Org. Chem.*, **36**, 769 (1971)). [e] Not determined.

anisyl phosphate was irradiated, the only coupling products observed were 4,4′-dimethylbiphenyl (56% yield, 24% conversion) and 4,4′-dimethoxybiphenyl (66% yield and conversion). We conclude that, in common with the photodecarboxylation of aryl carboxylates,[5] the formation of biaryl is intramolecular and occurs either in a concerted fashion, or between fragments very tightly contained within a solvent cage.

The data in Table I show that electron-donating substituents enhance both the chemical and quantum yields of the biaryl coupling products. The low yield of bimesityl, however, probably indicates a steric effect. The reactions of a set of "mixed" aryl phosphates are illustrated in eq 3–5. Here there is seen a partition between two possible coupling products which are formed in ratios significantly different from that expected if the groups coupled randomly. In each case there is a clear preference for the coupling of the more electron rich groups, which accords with the substituent effect already noted. The data suggest that the aromatic rings become charge deficient during the reaction and lead us to represent the excited state as an internal charge-transfer complex such as I.[6,9]



(3)



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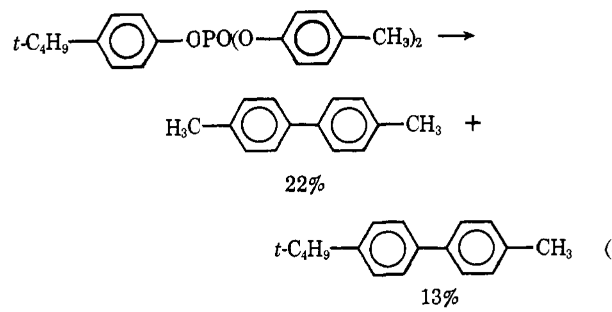
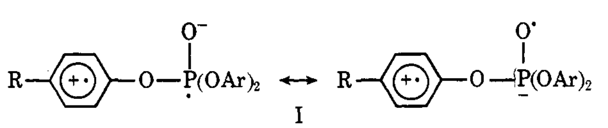


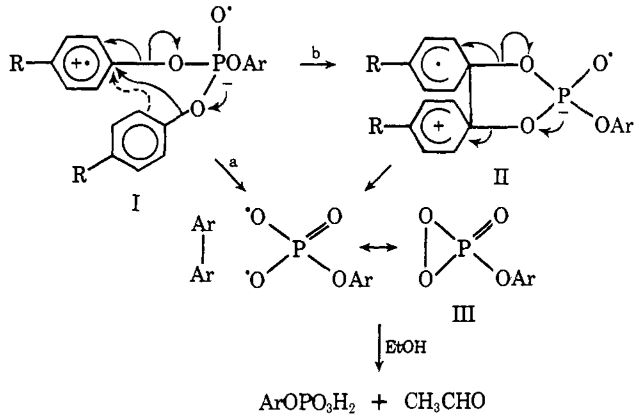
(5)



I

The collapse of I in a single step (path a, solid arrows in Scheme I) leads directly to the product biaryl along with the "peroxidized" phosphorus species III. Escape of III into the solvent ethanol leads, by reduction, to the monoaryl phosphate isolated. Furthermore, when the solvent is benzene, it is easily seen how III can add to a solvent molecule to produce a mixed phenyl aryl phosphate which, upon reexcitation, leads to a mixed biaryl.[10] Although the collapse of I can be envisioned as a direct process (path a), there is some reason to believe that the production of III may involve an intermediate such as II (path b, dotted arrow). A major reason for this postulation is to explain why *alkyl* aryl coupling is not observed when aryl dialkyl phosphate

Scheme I



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(5) R. A. Finnegan and D. Knutson, *J. Amer. Chem. Soc.*, **89**, 1970 (1967).

(6) The phosphoryl group has been observed to function as a donor in charge transfer;[7,8] however, we are unaware of previous indications that it might also serve as an acceptor. We are seeking independent evidence for this behavior.

(7) H. Tsubomura and J. M. Klingman, *J. Amer. Chem. Soc.*, **82**, 1314 (1960).

(8) A. S. Bailey and J. M. Evans, *J. Chem. Soc. C*, 2105 (1967).

(9) The fact that the reaction is almost completely quenched when the solvent is changed to ether is also consistent with the formation of a polar intermediate such as I or II.

(10) Thus, the photolysis of tri-*p*-cresyl phosphate in benzene solution is slow (up to 69% recovery of starting material after 5 hr), but there was obtained 4–5% of the 4,4′-dimethylbiphenyl. In addition, however, there was obtained 2–3% of the *monomethyl* compound, 4-methylbiphenyl!

esters are irradiated.[11] Clearly, an alkyl group could not function as a stable bridging group as required for the second aryl ring in II. In addition, the intermediacy of III fits very nicely with the results obtained for the unsymmetrical triaryl phosphates in which the rings bearing electron donating groups selectively couple. Additional work on the scope and mechanism of phosphate ester photoreactions is currently in progress.

(11) R. A. Finnegan and J. A. Matson, results to be published shortly. Diaryl alkyl phosphates, however, do give the biaryl on photolysis and we are studying this reaction as a potentially convenient photodeblocking step in monoalkylphosphoric acid synthesis.

(12) This article was prepared while the senior author was Guest Professor at the Institut für Pharmazeutische Arzneimittellehre der Universität München, and he wishes to thank the Directors and their colleagues for their hospitality during this period.

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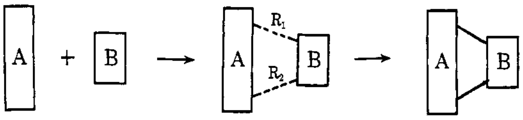
Received February 26, 1972

On the Existence of Symmetric Transition States for Cycloaddition Reactions

Sir:

A cycloaddition is a bimolecular reaction in which two (or more) bonds are formed. For cases in which the two bonds are equivalent (of equal length and type) in the cycloadduct, the question often arises as to whether or not these bonds are equivalent in the transition state as well. Is the transition state symmetric?



1

Let us assume that there exist symmetry elements such as a C_2 axis and/or a mirror plane which relate these bonds to one another in both the reactant (two isolated yet properly oriented molecules A and B in **1**) and product, and let us consider only geometry variations between reactant and product which preserve this symmetry. If there is a potential energy barrier to the reaction, then it follows that there will be at least one intermediate geometry which is a point of zero potential energy gradient within this symmetry (a stationary point) and which has a totally symmetric direction of negative curvature (the decomposition direction). Moreover, this point must also be a stationary point on the complete potential energy surface since the potential energy gradient is totally symmetric.[1] Such a structure is our candidate for the symmetric transition state. For the cycloaddition reaction the direction of negative curvature will generally have a large contribution from the symmetric stretching motion of the two bonds R_1 and R_2. It is therefore entirely reasonable to assume that the potential energy will decrease if the two bonds are simultaneously stretched (or shrunk) from their value at this stationary point.

Let us now inquire whether or not such a symmetric point is in fact a transition state, irrespective of its being "allowed" or "forbidden" by the Woodward–Hoffmann rules.[2] Murrell and Laidler have shown that a transition state must be a stationary point which has one and only one independent direction of negative curvature.[3] In other words, the force constant matrix at the transition state must have a single negative eigenvalue. If we assume that the two bond lengths R_1 and R_2 in **1** are the only degrees of freedom of importance here, then the force constant matrix can be represented as a 2×2 with diagonal elements $K = \partial^2E/\partial R_1^2 = \partial^2E/\partial R_2^2$ for the bond stretching force constants and $K' = \partial^2E/\partial R_1\partial R_2$ for the interaction constant. The eigenvalues of this matrix are $K + K'$ for the symmetric direction and $K - K'$ for the nonsymmetric direction. If $K + K'$ is negative, as in the symmetric stationary point for the cycloaddition, then $K - K'$ will also be negative provided that $|K'| < |K|$. The eigenvalues of the 2×2 force constant matrix are upper bounds on the lowest two eigenvalues of the complete force constant matrix[4] so that if $|K'| < |K|$, then the complete force constant matrix must have at least two negative eigenvalues. If this is true for each symmetric stationary point, then the transition state for the cycloaddition will be nonsymmetric.

Although it is true that interaction force constants are generally much smaller in magnitude than the corresponding stretching force constants in stable molecules, there is no reason to suppose that this will also be the case at other stationary points of the potential energy.[5] It seems reasonable, however, that the magnitude of K' will decrease as the number of intervening bonds in A and B increase, whereas the stretching constant K would be expected to be roughly independent of the distance between R_1 and R_2. Thus for $n + m$ cycloadditions, the likelihood of the transition state being nonsymmetric will increase as n and m increase.

To shed some quantitative light on this matter, we have calculated the geometries and force constants of four such symmetric points for cycloaddition reactions on MINDO/2[6] potential surfaces using a previously described method[7] of locating and identifying transition states: a "forbidden" (C_{2v} symmetry) structure for the addition of methylene to ethylene, an "allowed" (C_2 symmetry) and a "forbidden" (D_{2h} symmetry) structure for the dimerization of ethylene, and an "allowed" (C_s symmetry) structure for the ethylene and butadiene Diels–Alder reaction. The details will be given in a full paper. The most important result is that, in every case, the force constant matrix had two (or more) negative eigenvalues: one corresponding to the symmetric stretch of the two bonds being formed and the other

(1) J. W. McIver, Jr., and A. Komornicki, *Chem. Phys. Lett.*, **10**, 303 (1971).

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(3) J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.*, **64**, 371 (1968).

(4) This can be proved along the same lines as the analogous theorem for configuration interaction calculations of electronic states: *cf.* J. K. L. MacDonald, *Phys. Rev.*, **43**, 830 (1933).

(5) It is not the case, in fact, in the linear H_3 transition state. Here, the decomposition direction is asymmetric and the condition $|K'| < |K|$ gives rise to a "well at the top of the pass" which was found in earlier semiempirical studies and some more recent *ab initio* calculations [*e.g.*, H. Conroy and B. L. Bruner, *J. Chem. Phys.*, **42**, 4047 (1965)]. However, more accurate calculations reveal that this structure is a saddle-point with $|K'| > |K|$ [H. Conroy and B. L. Bruner, *ibid.*, **47**, 921 (1967)].

(6) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 3854 (1970).

(7) J. W. McIver, Jr., and A. Komornicki, *ibid.*, **94**, 2625 (1972).