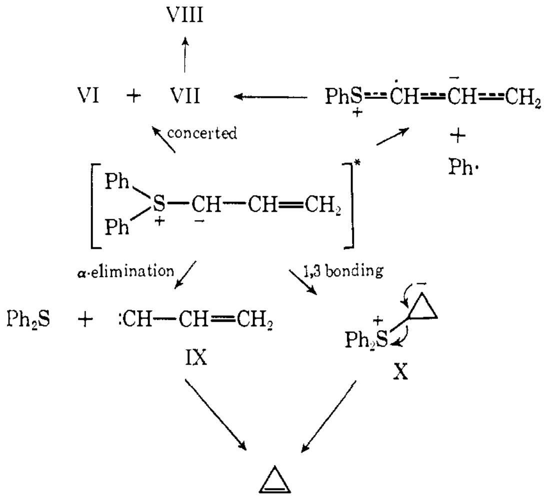
Scheme II. Mechanistic Interpretations



was not unexpected since base-catalyzed double bond isomerizations proceed facilely in such systems.

The formation of the Diels–Alder adduct III demonstrates the intermediacy of cyclopropene. However, such a discovery does not unambiguously indicate the intermediacy of the carbene IX. Alternatively, 1,3 bonding in the ylide to generate the cyclopropyl anion X followed by β elimination also yields cyclopropene. The great endothermicity associated with such a ring closure in the present case (going from a highly stabilized anion to a highly localized charge-separated species) either suggests the improbability of such a path or that 1,3 bonding occurs during internal conversion (*i.e.*, as the energy of the excited state dissipates by nonradiation processes). Such a ring closure is unprecedented. The apparent ability of other sulfur ylides to undergo α elimination during photolysis suggests the likelihood of the carbene pathway in the present case. The present results clearly rule out the intermediacy of carbenes in thermal decompositions of sulfur ylides. The present results also illustrate the utility such α eliminations may play in synthesis since the yield of trapped cyclopropene (25% yield based on ylide) is greater than other corresponding α eliminations (*e.g.*, allyl chloride or vinyldiazomethane). Since the spirodiene III can be demonstrated to trap only about one-third to one-half of the formed cyclopropene, the actual yield of such an α elimination is much higher than that of the isolated adduct.

Acknowledgment. We wish to express our gratitude to the National Institutes of Health for their generous support of our work.

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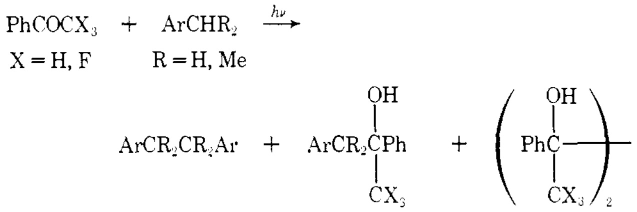
Photoreduction of α-Trifluoroacetophenone by Alkylbenzenes. Another Charge-Transfer Process

Sir:

Although photoreduction of ketones is probably the most studied of photochemical reactions, there have been relatively few studies of the inductive effects of substituents on excited state reactivity.[1] We have compared the behavior of α-trifluoroacetophenone to that of acetophenone itself[1,2] and find that the excited triplet of the former is photoreduced by electron transfer from such weak donors as alkylbenzenes.

The actual reduction proceeds similarly for both ketones, in that bibenzyls, pinacols, and cross-coupling products account for all the reacted ketone. Quantum yields of product formation were measured for both ketones in degassed benzene solutions as a function of concentration of toluene, cumene, and p-xylene. Results plotted according to eq 1 gave linear plots with the slopes and intercepts indicated in Table I. Y_{BB} represents the actual yield of bibenzyl; P, the probability that intermediates other than the excited state proceed on to products rather than reverting to ground states of reactants; [S], the concentration of alkylbenzene; k_d, the rate of radiationless decay of the ketone triplet; k_r, the rate constant for interaction of ketone triplet with substrate. Reduction of both ketones at 3660 Å was quenched with naphthalene at various concentrations of p-xylene. Stern–Volmer plots were linear, as were plots of $1/\tau$ (calculated from the S–V slopes) *vs.* [S], the slopes of which equal k_r. The k_r values for the other substrates were determined from the measured k_d/k_r values and the assumed constant value of k_d.



$$\mathrm{PhCOCX_3} + \mathrm{ArCHR_2} \xrightarrow{h\nu} \mathrm{ArCR_2CR_2Ar} + \mathrm{ArCR_2}\underset{\mathrm{CX_3}}{\overset{\mathrm{OH}}{\mathrm{CPh}}} + \left(\mathrm{Ph}\underset{\mathrm{CX_3}}{\overset{\mathrm{OH}}{\mathrm{C}}}\!-\!\right)_2$$

$$\mathrm{X = H, F} \qquad \mathrm{R = H, Me}$$

$$\Phi_{BB}^{-1} = Y_{BB}^{-1}P^{-1}\left(1 + \frac{k_d}{k_r[S]}\right) \tag{1}$$

$$1/\tau = k_d + k_r[S] \tag{2}$$

Table I. Kinetic Data for Photoreduction of Acetophenone and α-Trifluororacetophenone by Alkylbenzenes in Benzene

Ketone	Substrate	Y_{BB}	$Y_{BB}P^a$	k_d/k_r^b	k_r, 10^6 M^{-1} sec$^{-1\,c}$	k_d, 10^6 sec$^{-1\,d}$
$PhCOCH_3$	p-Xylene	0.44	0.10	1.0	0.70^c	0.7 (0.5)
$PhCOCH_3$	Cumene	0.39	0.18	2.5	0.28	0.7
$PhCOCH_3$	Toluene	0.39	0.13	5.8	0.12	0.7
$PhCOCF_3$	p-Xylene	0.35	0.04	0.09	97.0^c	9.0 (7.0)
$PhCOCF_3$	Cumene	0.34	0.06	2.7	3.3	9.0
$PhCOCF_3$	Toluene	0.32	0.05	1.2	7.5	9.0
$PhCOCF_3$	Toluene-α-d_3	0.31	0.015	1.2	7.5	9.0

[a] Reciprocal of intercept of plots according to eq 1. [b] Slope/intercept of plots according to eq 1. [c] Slope of plots according to eq 2. [d] Values in parentheses are the intercepts of plots according to eq 2.

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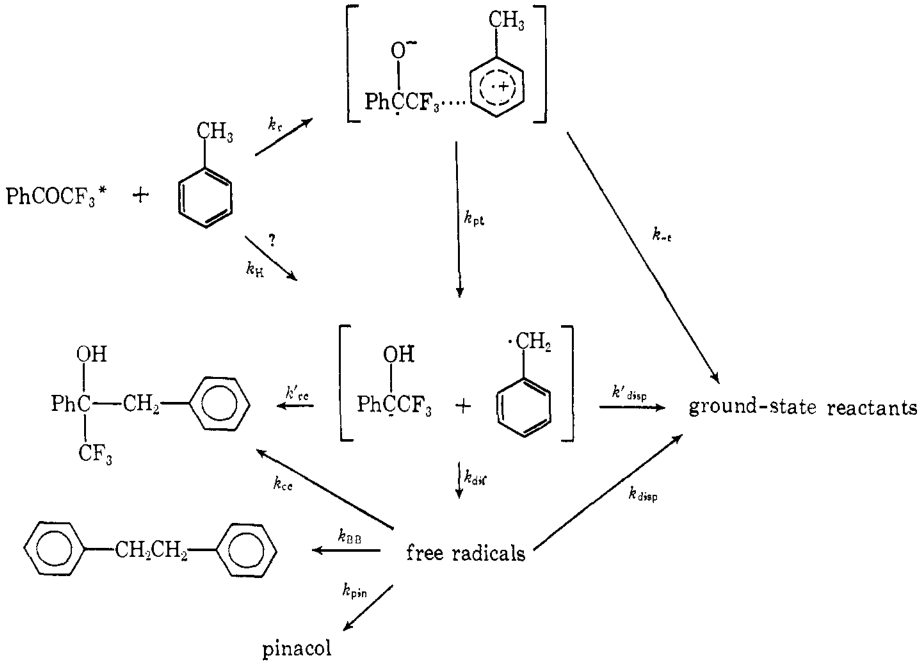
(1) For one example, see N. C. Yang and R. Dusenbery, *Mol. Photochem.*, **1**, 159 (1969).

(2) For previous studies on acetophenone, see (a) S. G. Cohen and B. Green, *J. Amer. Chem. Soc.*, **91**, 6824 (1969); (b) C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).

Scheme I



The reactivity of triplet acetophenone toward the different substrates agrees with that predicted by previous studies.[1-3] The reactivity of triplet trifluoroacetophenone is distinctly different in two regards: k_r values are two orders of magnitude larger than for acetophenone itself and they are independent of the benzylic C–H bond strength. Moreover, maximum quantum yields are less than half as large as with acetophenone.

Such marked differences in behavior suggest different photoreduction mechanisms for the two ketones. Triplet acetophenone's sensitivity to C–H bond strength indicates direct hydrogen atom abstraction. Triplet trifluoroacetophenone apparently interacts with the benzene ring itself, since there is no deuterium isotope effect on k_r, and cumene is less reactive than toluene.[4] Our results prompt us to suggest the following scheme (Scheme I) involving a primary charge-transfer interaction.

This scheme is similar to the charge-transfer mechanism suggested for the photoreduction of ketones by amines[2a,5] except that a π donor rather than an n donor is involved.

The lower P values observed with trifluoroacetophenone presumably signify that back electron transfer (k_{-r}) is as fast as proton transfer (k_{pt}). The 3.3-fold deuterium isotope effect on P is further evidence for this competition and indicates a minimum k_{pt}^H/k_{pt}^D value of 5 (if the isotope effect on radical disproportionation is ignored).

We have also studied the phosphorescence of trifluoroacetophenone at 77°K.[6] Emission decay was exponential (unlike that reported previously[7]) with a 57-msec lifetime in hydrocarbon glasses (0–0 band at 70.9 kcal) and a 200-msec lifetime in ethanol glass (0–0 band at 70.0 kcal). We take these observations to mean that the L_a π,π^* triplet lies slightly below the n,π^* triplet. However, they lie so close together that they must both be populated at room temperature. Both n,π^* and π,π^* triplets apparently can be reduced by charge transfer from amines.[8] Therefore, both triplet states of trifluoroacetophenone may be reacting with the aromatic substrates. The observed rate constant is then expressed by eq 3, where X_n and X_π are the equilibrium concentrations of n,π^* and π,π^* triplets. Note that a

$$k_r = X_n k_r^n + X_\pi k_r^\pi + X_n k_H \qquad (3)$$

third term is included in eq 3 for direct benzylic hydrogen abstraction by the n,π^* triplet, a small amount of which may compete with the charge-transfer process since the trifluoro ketone is photoreduced smoothly by cyclohexane and by isopropyl alcohol. We are now investigating the kinetics of these processes which cannot involve charge transfer.

Finally, the large k_d value for the trifluoro ketone probably reflects charge-transfer quenching of the triplet by the benzene solvent, with a rate constant of $0.8 \times 10^6\ M^{-1}\ \text{sec}^{-1}$. Each methyl group on the benzene ring increases this rate constant by an order of magnitude. The rapid decay rate of triplet ketones in benzene[9] apparently is real[10,11] and has been attributed to radical-like addition.[11] We feel that a charge-transfer interaction is more likely. In that event a small fraction of photoreduction by alkyl aromatics may proceed by charge-transfer intermediates. Such behavior would explain the low P values observed for acetophenone; for example, only 0.23 with p-xylene *vs.* 0.33 with

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[3] Bibenzyl quantum yields are much lower with toluene-α-d_3 than with toluene itself, but a plot according to eq 1 curves upward, presumably because unimolecular radical scavenging reactions (by solvent or residual oxygen) begin to compete with coupling at low steady-state radical concentrations.

[4] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr. (*ibid.*, **91**, 6830 (1969)) have reported the same effect in the cobaltic acetate oxidation of alkylbenzenes.

[5] P. J. Wagner and A. E. Kemppainen, *ibid.*, **91**, 3085 (1969).

[6] We thank Professor Alfred Haug of the MSU-AEC Plant Research Laboratory for the use of his equipment.

[7] R. N. Griffin, *Photochem. Photobiol.*, 7, 159 (1968).

[8] (a) S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, **72**, 3782 (1968); (b) A. Padwa, W. A. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 1857 (1969).

[9] J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

[10] W. D. K. Clark, A. D. Litt, and C. Steel, *ibid.*, **91**, 5413 (1969).

[11] J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, *ibid.*, **92**, 410 (1970).

toluene. Such large fractions of disproportionation between radicals would be unusual, although not impossible.[12]

Acknowledgment. This work was partially supported by a grant from the National Science Foundation.

[12] P. J. Wagner and H. N. Schott, *J. Amer. Chem. Soc.*, **91**, 5383 (1969).

[13] Alfred P. Sloan Fellow, 1968–1970; to whom correspondence should be addressed.

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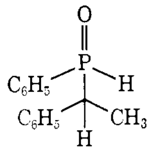
Lithium Aluminum Hydride Induced Stereomutation of Secondary Phosphine Oxides[1]

Sir:

Recent reports[2,3] that the synthesis of optically active *secondary* phosphine oxides is accomplished by lithium aluminum hydride (LAH) reduction of diastereomerically enriched menthyl phosphinates appear to be at variance with our observation[4] that *tertiary* phosphine oxides undergo stereomutation in the presence of LAH *prior* to reduction. We now wish to report a resolution of this apparent discrepancy.

Diastereomers (**a** and **b**) of phenyl-α-phenylethylphosphine oxide (**1**)[5] were separated by a combination of column chromatography (silica gel, benzene–chloroform) and fractional crystallization (benzene–hexane). Diastereomeric compositions of **1** were measured by pmr spectroscopy.[7]



1

Upon treatment with LAH at room temperature in tetrahydrofuran or diethyl ether (0.35 mmol of LAH/mmol of **1**), followed by hydrolysis with aqueous ammonium chloride, each diastereomer of **1** was rapidly (<30 sec) transformed into an approximately equimolar mixture of **1a** and **1b**. Although some decomposition occurred, recovery of **1** was at least 75–80%. Reaction of **1b** with an excess of LAH (2 mmol of LAH/mmol of **1**) also gave an approximately equimolar mixture of **1a** and **1b** in <30 sec, but recovery of epimerized **1** was only 40–50%.[8] Reaction of **1** with less than 0.35 mmol of LAH/mmol of **1** resulted in incomplete epimerization.[9,10]

The observation of stereomutation of **1** with LAH is readily accommodated by a mechanistic model similar to that which was invoked[4] for the tertiary phosphine oxides: addition–elimination of hydride reagent to the phosphine oxide.[11] In contrast to tertiary phosphine oxide systems, however, pseudorotation of the postulated trigonal-bipyramidal intermediate ($[R_1R_2HH'P(OAlL_3)]Li$) is not required to account for epimerization of secondary phosphine oxides. In the intermediate in which both hydrogens are apical, or in the three intermediates in which both hydrogen atoms occupy equatorial positions, addition of H followed by loss of H′ leads directly to epimerization. For the other three isomers, such hydride exchange does not directly lead to epimerization.

The LAH-induced epimerization of **1** clearly reveals that LAH reduction of phosphinates is not a suitable method for the preparation of optically active secondary phosphine oxides. Repeated attempts in this laboratory to obtain optically active benzylphenylphosphine oxide (**2**), employing conditions identical with those previously described,[2] have provided only racemic **2**.[14] Furthermore, **1a** and **1b** do not undergo epimerization in methanolic solutions of dilute (0.05 *M*) hydrogen chloride or sodium methoxide during a 12-hr period.[15] The reported[2,3] racemization in such

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[1] This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

[2] T. L. Emmick and R. L. Letsinger, *J. Amer. Chem. Soc.*, **90**, 3459 (1968).

[3] O. Červinka, O. Bělovský, and M. Hepnerová, *Chem. Commun.*, 562 (1970).

[4] P. D. Henson, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 5645 (1969).

[5] Alkylation[6] of the sodium salt of *n*-butyl phenylphosphinate with α-phenylethyl bromide, followed by treatment with phosphorus pentachloride, afforded phenyl-α-phenylethylphosphinyl chloride, which yielded **1** upon reaction with lithium tri-*tert*-butoxyaluminum hydride.

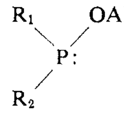
[6] G. M. Kosolapoff, *J. Amer. Chem. Soc.*, **72**, 4292 (1950).

[7] The pmr spectrum of the diastereomer (**1a**) eluted in the first fractions featured: CH_3, dd, τ 8.39, $^3J_{PH} = 17.5$ Hz, $^3J_{HH} = 7.2$ Hz; PH, dd, τ 2.73, $J_{PH} = 468$ Hz, $^3J_{HH} = 3.3$ Hz. The pmr spectrum of the other diastereomer (**1b**), mp 110–111°, featured: CH_3, dd, τ 8.41, $^3J_{PH} = 17.5$ Hz, $^3J_{HH} = 7.2$ Hz; PH, dd, τ 2.62, $J_{PH} = 468$ Hz, $^3J_{HH} = 1.3$ Hz. Diastereomeric compositions were determined by integration of the low-field half of the characteristic PH resonances. *Anal.* of **1**: Calcd for $C_{14}H_{15}PO$: C, 73.03; H, 6.57; P, 13.45. Found: C, 72.77; H, 6.86; P, 13.50.

[8] A sample of **1** recovered from a reaction mixture of **1b** and LAH (2 mmol of LAH/mmol of **1**) which had been quenched with D_2O showed no exchange of the benzylic hydrogen. It follows that epimerization at the chiral carbon center cannot be responsible for the stereomutation.

[9] For example, treatment of **1b** with LAH (0.17 mmol of LAH/mmol of **1**) gave a 40/60 mixture of **1a**/**1b**.

[10] Some evolution of hydrogen was noted. While this observation suggests the possibility that stereomutation of **1** may in part occur by way of intermediate i, assuming that i is pyramidally unstable under the conditions of the reaction, such a mechanism is rendered less likely by the finding that no detectable hydrogen evolution occurred during the stereomutation of **1** by lithium tri-*tert*-butoxyaluminum hydride.



i

[11] That stereomutation of **1** is not significantly due to a process involving reduction to a secondary phosphine[12] followed by adventitious oxidation during work-up was shown by LAH treatment (0.18 mmol of LAH/mmol of **1**) of ^{18}O-labeled **1** (3.11 ± 0.15 atom % ^{18}O/mol).[13] The recovered phosphine oxide contained 2.79 ± 0.15 atom % ^{18}O/mol.

[12] Secondary phosphines can be obtained by treatment of the corresponding phosphine oxide with excess LAH (L. Horner, H. Hoffmann, and P. Beck, *Chem. Ber.*, **91**, 1583 (1958)).

[13] Prepared by treatment of **1** with an HCl-saturated solution of ^{18}O-enriched water (3.25 atom % ^{18}O/mol) and dioxane (D. B. Denney, A. K. Tsolis, and K. Mislow, *J. Amer. Chem. Soc.*, **86**, 4486 (1964)).

[14] Treatment of (−)-menthyl benzylphenylphosphinate[2] with a twofold excess of LAH at 0° for 0.5 hr also gave racemic **2**, even though the starting ester proved to be epimerically stable under these conditions.

[15] The diastereomeric compositions of two different mixtures of **1a** and **1b** remained invariant upon successive treatment with methanol-*d* and methanol. Thus, hydrogen–deuterium exchange in **1** occurs with *retention* of configuration.