Table VI. Frequencies of Some Major C–H and C–D Stilbene Vibrations[a]

Stilbene-d_0		Stilbene-d_2		Stilbene-d_{10}		Stilbene-d_{12}		Tentative	
Trans	Cis	Trans	Cis	Trans	Cis	Trans	Cis	assignment[b]	
3040 (sh)	3040	3021	3040	*2272*	*2272*	*2273*	*2283*	Ar	stretch
		2994	3012						
3012	3000	*2222*	*2237*	3010	3000	*2237*	*2247* (*sh*)	Ol	stretch
1067	1068	1075	1071	*845*	*861*	*845*	*847*	Ar	in-plane bend
1030	1025	1027	1022	*824*	*820*	*824*	*823*		
756	693	758	693					Ar	out-of-plane bend
686		684							
960		*710*		960		*712*		Ol	out-of-plane bend

[a] Frequencies in cm^{-1}, estimated accuracy ±5 cm^{-1}. Frequencies for C–D vibrations are given in italics. [b] Aromatic and olefinic are abbreviated as Ar and Ol, respectively.

via probe and immersed in a water bath whose temperature was kept at 25 ± 1 or 60 ± 1°. A 200-W Hanovia high-pressure mercury lamp, whose output was filtered with a cylindrical uranium glass tube transmitting light of wavelengths longer than 320 nm, was employed.

Flash Kinetic Spectrophotometry. The apparatus for triplet lifetime measurements by flash kinetic spectrophotometry is similar to that used in earlier investigations.[13,50] Two xenon flashlamps (Model W3G20, Kemlite Laboratories) were connected in series and located on opposite sides of a cylindrically shaped, quartz dewar having plane windows on the bottom. The lower half of the dewar was transparent to the excitation light. The energy output of the flash lamps was variable between 200 and 400 J by selection of voltage on a 2-μF, low inductance, storage capacitor. Between the dewar and the flash lamps were positioned glass color filters (Corning 9863). The dc monitoring source was a 100-W high-intensity, point source, mercury arc lamp (Osram, HBO 100 W/2). Sample solutions were contained in cylindrical quartz cells having plane windows on the ends and positioned vertically in the center of the dewar and were cooled with either liquid nitrogen or a Dry Ice-acetone slurry. The dimensions of the cells were 100-mm optical length and 13-mm i.d. The cells were connected to bulbs where the solutions were contained during the degassing procedure. The collimated monitoring light reflected 90° from a plane mirror, passed through the sample cell, the bottom of the dewar, again reflected 90° from a plane mirror and focussed on the entrance slit of a Jarrell-Ash 0.25-m grating monochromator. An RCA 4463 photomultiplier tube, mounted on the exit of the monochromator, served as detector. The signal from the detector was dc coupled through a cathode-follower amplifier to a Tektronix Model 555 wide-band oscilloscope where it was displayed and recorded photographically.

The oscilloscope transparencies were enlarged in order to facilitate more precise measurement of the transient kinetics. The lifetimes of the transient species were measured by the recovery rate of the monitoring beam following completion of the excitation flash. Kinetic analysis was by the method of Linschitz and Sarkanen.[51]

---

[50] D. S. McClure, *J. Chem. Phys.*, **19**, 670 (1951).

[51] H. Linschitz and K. Sarkanen, *J. Amer. Chem. Soc.*, **80**, 4826 (1958).

Primary Interaction between Diaryl Ketone Triplets and Simple Alkenes. Isotope Effects

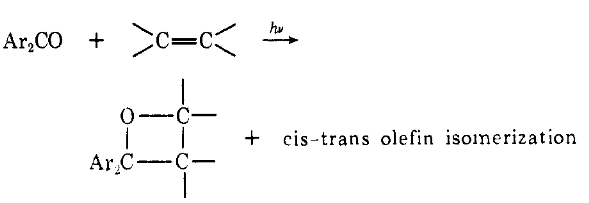
R. A. Caldwell,* G. W. Sovocool, and R. P. Gajewski

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850, and The University of Texas at Dallas, Dallas, Texas 75230. *Received September 18, 1972*

Abstract: The primary interaction between benzophenone triplet and simple alkenes is shown to be irreversible formation of a complex. The complex possesses substantial change-transfer character, with olefin as donor and ketone as acceptor. The complex has a finite (though undetermined) lifetime. Support for these conclusions derives from kinetic and quantum-yield studies with the isomeric butenes, and most importantly from the comparison of the results of an extensive study of secondary deuterium isotope effects with mechanistic models.

The photocycloaddition of aromatic carbonyl compounds to simple olefins, affording oxetanes, is an interesting and useful application of photochemistry to organic synthesis.[1-3] It is now a well-established reaction of broad scope. Several reviews of its applications and of related mechanistic studies are available.[4,5]

It is clear that several different mechanisms are possible. Ketone singlets can form oxetanes with olefins.[6-9] Although in some cases π,π* ketone excited



+ cis–trans olefin isomerization (1)

---

[1] E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39**, 341 (1909).

[2] G. Büchi, J. T. Kofron, E. Koller, and D. Rosenthal, *J. Amer. Chem. Soc.*, **78**, 876 (1956).

[3] S. G. Schroeter and C. M. Orlando, Jr., *J. Org. Chem.*, **34**, 1181 (1969).

[4] G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).

[5] D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

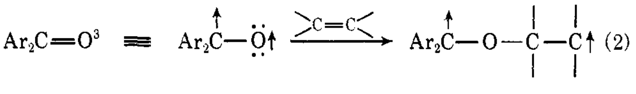
[6] N. C. Yang and W. Eisenhardt, *J. Amer. Chem. Soc.*, **93**, 1277 (1971).

[7] N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *ibid.*, **89**, 3950 (1967).

[8] N. J. Turro, P. A. Wriede, and J. C. Dalton, *ibid.*, **90**, 3274 (1968).

[9] N. J. Turro and P. A. Wriede, *ibid.*, **92**, 320 (1970).

states are thought to react,[10] the most common reactions involve ketones with n,π^* lowest triplets and simple alkenes.[5] This latter mechanism involves the addition of triplet ketone to the olefin, as an analog of an alkoxy radical addition, to produce a 1,4 biradical (eq 2) as the immediate precursor of oxetane.[5] The



$$\mathrm{Ar_2C{=}O^3} \equiv \mathrm{Ar_2\overset{\uparrow}{C}{-}\ddot{O}\uparrow} \xrightarrow{>C=C<} \mathrm{Ar_2\overset{\uparrow}{C}{-}O{-}C{-}C\uparrow} \quad (2)$$

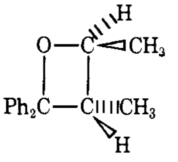
1

$$\mathbf{1} \longrightarrow \text{oxetane} \quad (3)$$

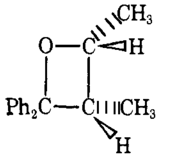
analogy between n,π^* carbonyl triplets and alkoxy radicals has been widely discussed.[5,11,12]

Arnold[5] has previously determined several basic features of the triplet state benzophenone:butene oxetane-forming reactions.

(1) Whether *cis*- or *trans*-2-butene is the reacting molecule, the same mixture of oxetanes **2** and **3** is



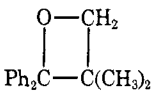
2



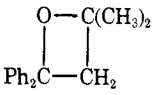
3

obtained (**2**:**3** $\simeq$ 6:1[13]). Biradical intermediates such as **1** are thus very strongly indicated.

(2) With isobutylene, the isomeric oxetanes **4** and **5** are formed in the ratio of 9:1. This fact, and other



4



5

related examples where carbons bearing radical-stabilizing groups preferentially are bonded in the product (as in **4**), led to the early suggestion of the "most stable 1,4 biradical" as a device for product prediction.[14] However, there are now numerous counter examples,[5] and enough quantitative work has been done to show that other factors must surely enter in determining product distributions.

(3) With 2-butene, cis–trans isomerization accompanies oxetane formation. The early work[15] did not establish whether isomerization resulted from bond rotation and β scission, *e.g.*, eq 4, or from triplet ex-

$$\mathbf{1} \longrightarrow \text{spin inversion} \longrightarrow \mathrm{Ph_2C{=}O} + \mathrm{>C{=}C<}\ \text{isomers} \quad (4)$$

citation transfer, and in fact suggested the latter. The importance of the oxetane-forming system as a relatively simple example of a bimolecular photochemical reaction prompted a more detailed examination.

Direct formation of a biradical as an elementary reaction of the ketone triplet with the olefin, eq 2, was generally accepted as the only possibility.[5] The evidence in favor of a biradical intermediate, however, did not preclude the possibility of an intermediate prior to the biradical. Equations 2a and 2b comprise a viable elaboration of eq 2.

$$\mathrm{Ph_2C{=}O^3} + \mathrm{C{=}C} \longrightarrow \mathrm{X} \quad (2a)$$

$$\mathrm{X} \longrightarrow \mathbf{1} \quad (2b)$$

A considerable body of recent evidence offers direct support for formation of excited-state complexes in a great many singlet-state systems.[16-21] Such excimers have long been known as the source of long-wavelength, concentration-dependent fluorescence for a number of aromatic hydrocarbons.[16] Amine–arene excited-state complexes are known similarly.[17,22] Cycloadditions of tetramethylethylene to *trans*-stilbene singlets occur with an excited state complex intermediate.[23] In a particularly apt analogy to the present case, the quenching of acetone singlets with fumaronitrile is believed to occur with the intermediacy of an excited-state complex.[8]

There has been a tendency in the literature to infer that triplet excited state complexes are similarly important.[24-28] The evidence, unfortunately, has been much more tenuous than that for singlet complexes. Direct observation is difficult since excited state complex phosphorescence is extremely rare.[16a] Corey,[29] utilizing substituent effects on relative reactivity, years ago inferred the intermediacy of a complex in the addition of alkenes to cyclohexenone. Similarly, substituent effects in the quenching of butyrophenone triplets with alkenes have suggested an excited-state complex.[30] In both these cases, change transfer was indicated; however, the possibility of a polar transition state in an elementary radical-like addition, *e.g.*, eq 2, exists, and these reults, while suggestive, are thus not completely conclusive. Our preliminary experiments utilizing secondary deuterium isotope effects[31-33] were designed to distinguish excitation transfer and biradical formation–β scission mechanisms in benzophenone-sensitized alkene isomerizations. Since the first results were not easily compatible with either simple mechanism, we examined the system in more

---

[10] L. A. Singer, G. A. Davis, and V. P. Muralidharan, *J. Amer. Chem. Soc.*, **91**, 897 (1969).

[11] C. Walling and V. Kurkov, *ibid.*, **88**, 4727 (1966).

[12] C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).

[13] The ratio given on p 372 of ref 5 is reversed: D. R. Arnold, private communication.

[14] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965.

[15] D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964).

[16] (a) Th. Forster, *Angew. Chem., Int. Ed. Engl.*, **8**, 333 (1969), and references therein; (b) B. Stevens, *Advan. Photochem.*, **8**, 161 (1971).

[17] E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 3586 (1970).

[18] A. K. Chandra and E. C. Lim, *J. Chem. Phys.*, **48**, 2589 (1968); **49**, 5066 (1968), and references therein.

[19] D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3679 (1972).

[20] G. N. Taylor and G. S. Hammond, *ibid.*, **94**, 3684 (1972).

[21] G. N. Taylor and G. S. Hammond, *ibid.*, **94**, 3687 (1972).

[22] (a) H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 839 (1969), and references therein; (b) H. Beens, H. Knibbe, and A. Weller, *J. Chem. Phys.*, **47**, 1183 (1967).

[23] O. L. Chapman and R. D. Lura, *J. Amer. Chem. Soc.*, **92**, 6352 (1970).

[24] P. DeMayo, *Accounts Chem. Res.*, **4**, 41 (1971).

[25] C. C. Wamser, G. S. Hammond, C. T. Chang, and C. Baylor, *J. Amer. Chem. Soc.*, **92**, 6362 (1970).

[26] H. Beens and A. Weller in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 203.

[27] I. G. Lopp, R. W. Hendren, P. D. Wildes, and D. G. Whitten, *J. Amer. Chem. Soc.*, **92**, 6440 (1970).

[28] J. K. Roy and D. G. Whitten, *ibid.*, **93**, 7094 (1971), appear to provide the soundest evidence for a triplet exciplex presently available.

[29] E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964).

[30] (a) I. Kochevar and P. J. Wagner, *ibid.*, **92**, 5742 (1970); (b) *ibid.*, **94**, 3859 (1972).

[31] R. A. Caldwell and G. W. Sovocool, *ibid.*, **90**, 7138 (1968).

[32] R. A. Caldwell and S. P. James, *ibid.*, **91**, 5184 (1969).

[33] R. A. Caldwell, *ibid.*, **92**, 1439 (1970).

detail. We suspected the intermediacy of an excited-state complex. We have thus compared our results against both the *direct biradical mechanism*, eq 2, and the *excited state complex mechanism*, eq 2a and 2b, with the hope of providing at least one clear case where direct biradical formation can either be demonstrated or vitiated.

Experimental Section

General. Vapor phase chromatographic analyses were performed on an F&M Model 700 instrument. Nuclear magnetic resonance spectra were performed on a Varian A-60A spectrometer. Mass spectra at low voltage were obtained on a Consolidated Model 21-103 mass spectrometer, and some 70-V spectra were obtained on an AEI MS-901 instrument.

Aromatic ketones were recrystallized from ethanol or ethanol-water until their melting points agreed with literature values: 4-trifluoromethylbenzophenone, 114–115.3°, lit.[34] 113–115°; 4,4-dimethoxybenzophenone, 142.7–144.3°, lit.[35] 142–144°; 4-benzoylpyridine, 70.5–72°; lit.[36] 71.5–72.5°. Benzophenone itself was recrystallized from ether and twice sublimed.

Benzene as solvent was described previously.[37]

Dichloroethylenes were purified by simple distillation of commercially available material, followed by preparative vpc on a 20% DC-200 silicone oil column.

***cis*- and *trans*-2-butenes and isobutylene**, obtained from Matheson Chemical Corp. as 99% pure, were used as received or were distilled slowly on a vacuum line from a pot maintained at Dry Ice temperature to a receiver maintained at liquid nitrogen temperature. When necessary for quantitative work, the olefins were purified further by preparative vpc on a 10% silver nitrate–15% benzyl cyanide column (BC/SN; either 0.25 in × 6 ft or $^3/_8$ in × 8 ft) at ambient temperature. These conditions were shown to separate the olefins from butadiene and isoprene and to separate the *cis*- and *trans*-2-butene isomers cleanly.

***cis*-2-Butene-*2,3-d*$_2$** was prepared by the reduction of 2-butyne with deuterium gas in the presence of Lindlar catalyst and quinoline.[38] From 0.042 mol of butyne allowed to remain in contact with the catalyst overnight in an otherwise evacuated system was obtained, after preparative vpc on BC/SN, 0.015 mol of *cis*-2-butene-*2,3-d*$_2$. Analysis by nmr showed only a slightly broadened singlet for the allylic hydrogens. Mass spectral analysis at low voltage showed 92.8% d_2, 5.9% d_1, 0.24% d_0, 0.7% d_3, and 0.36% d_4.

trans*-2-Butene-*2-d has been previously described.[39]

3-Methyl-2-pentene-*2-d* was prepared by the *trans*-2-butene-*2-d* procedure,[39] utilizing commercially available 3-methyl-2-pentene as the reactant. The Grignard formation from 2-bromo-3-methyl-2-pentene was inefficient. It resulted in 33% yield of titrated Grignard and *ca.* 10% yield of deuterated olefin after D_2O quenching and preparative vpc.

The olefin isomers could be cleanly separated at 22° on a 12 ft × $^3/_8$ in. polypropylene glycol column (18% on 60–80 mesh Chromosorb P).

Isobutylene-*β,β-d*$_2$ was prepared essentially by the procedure published for isobutylene-*β*-^{14}C.[40] The starting 1,1-dideuterio-2-methylpropanol was prepared by lithium aluminum deuteride reduction of methyl isobutyrate in dry ether. Final purification of the isobutylene involved multiple slow bulb-to-bulb distillations from a reservoir maintained in a Dry Ice–acetone bath to a receiver cooled in liquid nitrogen. The only signals observed in the nmr spectrum of this material were a methyl singlet at τ 8.31 and an extremely weak signal in the vinyl region. Mass spectrometric analysis indicated the material to be 97.8% d_2 and 2.2% d_1.

For Stern–Volmer experiments, isobutylene was further purified by preparative vpc on BC/SN.

Photolyses in benzene were performed preparatively in a standard well using a Hanovia 450-W medium-pressure lamp and a Corning 3320 uranium glass filter sleeve. Quantitative photolyses were performed with ferrioxalate actinometry in a merry-go-round apparatus with a Corning 7-83 filter to isolate the 3660 Å region. For both isotope effect and quantum-yield studies, solutions were prepared in thrice-outgassed and sealed-off 13-mm Pyrex ampoules. Some isotope effects were performed in 10-mm Pyrex ampoules with no other filter. Only sensitizer absorbed light in all experiments.

Preparative photolyses with benzophenone afforded the known[5] oxetanes with 2-butene and isobutylene. Chromatography on base-washed activity III alumina, and recrystallization from hexane, afforded from isobutylene 2,2-diphenyl-3,3-dimethyloxetane: nmr δ 1.09 (s, 6 H), 4.21 (s, 2 H), 7.3 (m, 10 H). A minor component, nmr δ 1.29 (s) and 3.24 (s), ratio *ca.* 3:1, was found in the same chromatography fractions as *ca.* 8% of the oxetane. It was presumed to be the isomeric 2,2-diphenyl-4,4-dimethyloxetane[5] and was not isolated.

From 2-butene (which underwent cis–trans isomerization at a rate moderately faster than oxetane formation) was obtained a mixture of the cis and trans isomers of 2,2-diphenyl-3,4-dimethyloxetane. The predominant trans isomer was never obtained free from the cis; however, the following nmr assignments could be obtained from the mixtures with no difficulty. For trans: 3-CH_3, δ 0.87 (d, J = 7 Hz); 3-H, δ 3.1 (quintet, J = 7 Hz); 4-CH_3, δ 1.3 (J = 6 Hz); 4-H, δ 4.35 (quintet, J = 6 Hz). For cis: 3-CH_3 (buried under trans-3-CH_3); 3-H, δ 3.42 (J = 7.5 Hz); 4-CH_3, δ 1.23 (d, J = 6 Hz); 4-H, δ 4.85 ($J \simeq$ 6.5 Hz).

Quantum yields were studied in benzene solution or (see text) in neat isobutylene. Analysis for 2-butene isomerization was performed by vpc on BC/SN. The starting isomer, purified by preparative vpc, was metered into an outgassed ampoule containing other reactants and solvent by standard gas-handling techniques (ideal gas assumed). Irradiations were carried out to low conversion (typically 7% or less) to ensure that the total 2-butene was essentially constant. Material balance of 2-butene was thus assumed, and after controls to show that evaporation of these low-boiling materials from the opened ampoules during repetitive analyses introduced no problems, yields of isomer were calculated from the cis:trans ratios.

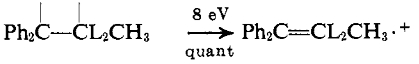
Analyses for oxetanes were performed by nmr. The assumption was made that aromatic hydrogens were conserved in the reaction. The nmr spectrum in each reaction studied required $\phi < 0.01$ for formation of any other new products but oxetanes.

Isotope effects involved several different methods of deuterium analysis. Typically in olefin isomerization a mixture, approximately 1:1, of labeled and unlabeled material was irradiated in the presence of benzophenone, the resultant olefin mixture was separated by preparative vpc into its component isomers, and both isomers were compared *via* low-voltage mass spectrometry with starting material. Accuracy of these analyses was *ca.* ±1% in all cases.

Deuterium content of 2,2-diphenyl-3,3-dimethyloxetane was determined in the reaction mixture by nmr integration of the methylene proton signal relative to the methyl signal; this analysis was not changed by chromatography of the reaction mixture recrystallization of the product from hexane, or further chromatography of recrystallized material. The average of *ca.* 30 scans allowed a precision of ±1.5% to be obtained.

The isotope effect on the *total* quenching of benzophenone triplet by isobutylene was measured by careful vpc analysis in Stern–Volmer plots for the quenching of *trans*- to *cis*-dichloroethylene isomerization by either unlabeled or pure dilabeled isobutylene.

The oxetanes from 2-butene could be analyzed mass spectrometrically both for the extent and the position of deuteration, owing to the following exceptionally clean mass spectral fragmentation at low voltage.



$$\mathrm{Ph_2C(-CL_2CH_3)-O-CL_1CH_3}\cdot^{+} \xrightarrow[\text{quant}]{8\ \text{eV}} \mathrm{Ph_2C{=}CL_2CH_3}\cdot^{+}$$

m/e 194, L_2 = H
m/e 195, L_2 = D

For monolabeled 2-butene, mass spectrometric analysis of reaction mixtures, nmr analysis (by integration of the two methine quartets) of chromatographed and recrystallized (major) oxetane, and mass spectrometric analysis of the purified material were all performed on two samples. The results (Table I) are taken as *prima facie* evidence that mass spectrometric (MS) analysis of reaction mixtures is a satisfactory criterion of deuterium content. The majority of

---

(34) S. Rossi and W. Batta, *Farmaco, Ed. Sci.*, **16**, 326 (1961).

(35) I. A. Kaye, H. C. Klein, and W. J. Burdant, *J. Amer. Chem. Soc.*, **75**, 745 (1953).

(36) K. E. Crook and S. M. McElvain, *ibid.*, **52**, 4006 (1930).

(37) R. A. Caldwell, *J. Org. Chem.*, **34**, 1886 (1969).

(38) H. Lindlar and R. Dubuis, *Org. Syn.*, **46**, 89 (1966).

(39) R. A. Caldwell, *J. Org. Chem.*, **35**, 1193 (1970).

(40) W. Reeve, D. H. Chambers, and C. S. Prichett, *J. Amer. Chem. Soc.*, **74**, 5370 (1952). These authors demonstrated that label scrambling was insignificant.

Table I

	Sample 1 4-D/3-D	Sample 2 4-D/3-D
MS, reaction mixt	1.222 ± 0.008	1.151 ± 0.005
Nmr, recrystallized	1.25 ± 0.04	1.158 ± 0.012
MS, recrystallized	1.232 ± 0.006	1.159 ± 0.008

these isotope effects were thus done directly using the reaction mixture.

The deuterium contents of mixtures of labeled and unlabeled 2-butenes were measured mass spectrometrically at low voltage. It was necessary to analyze *ca.* 1 mg of total isomerized butene for deuterium content in these cases. Appropriate controls ensured that the manipulation of such small samples *via* preparative vpc, collection on a glass wool plug at liquid nitrogen temperature, and transfer on a vacuum line to a reservoir compatible with the MS inlet system did not affect this deuterium analysis.

Isomerization of labeled 3-methyl-2-pentene was followed similarly. In this case, scrupulous precautions were necessary to ensure that olefin from one run did not interfere with that from the next by retention in the stopcock grease.

Results and Discussion

In addition to the usual measurements of quantum yields, rate constants, and substituent effects, we have performed a thorough study of secondary deuterium isotope effects in both oxetane formation and 2-butene isomerization. In addition, we have measured the isotope effect for total quenching of benzophenone triplet by isobutylene. We examine the results in terms of the biradical and the complex mechanisms.

Quantum yields of the various products were determined (*cf.* Table II). Of special interest were those for the products from the 2-butene isomers and benzophenone. The sum of $\phi_{c\rightarrow t} + \phi_{t\rightarrow c} = \phi_{\text{oxetane}}$ observed is 0.54 ± 0.04, *significantly less than unity.* The biradical mechanism must at least be modified, since it allows for no inefficiency. Note that for a freely rotating biradical, if formed from each olefin quantitatively, $\phi_{c\rightarrow t} + \phi_{t\rightarrow c}$ and ϕ_{oxetane} are simply the fractions of each product that the biradical affords and thus must sum to unity.

Table II. Quantum Yields for the Products of the Reactions of Benzophenone Triplet with Butenes in Benzene

	$\phi_{\text{cis}\rightarrow\text{trans}}$	$\phi_{\text{trans}\rightarrow\text{cis}}$	ϕ_{oxetanes}
cis-2-Butene (0.3 *M*)	0.30 ± 0.01		0.10 ± 0.01
trans-2-Butene (0.3 *M*)		0.14 ± 0.005	0.1 ± 0.03
Isobutylene (0.5 *M*)			0.087 ± 0.003
Isobutylene (neat)			0.091 ± 0.003[a]
Isobutylene (neat) H_2/D_2 = 1:1			0.087 ± 0.003[b]

[a] Same at 10 and 80% of benzophenone reacted. [b] Independent of extent of conversion from 8 to 67% of benzophenone reacted.

On the other hand, the complex mechanism is easily consistent with this observation. Rapid bimolecular induced radiationless decay, eq 2c in the present case,

$$\mathrm{Ph_2C{=}O^3 + C{=}C \longrightarrow complex \longrightarrow Ph_2C{=}O + C{=}C} \quad (2c)$$

appears so far to be a probable common property of the various postulated triplet excited-state complexes.[41,42]

The observed oxetane quantum yield with isobutylene is similarly low. However, in this case no estimate of total biradical quantum yield is possible since there is no isomerization and thus no monitor of the amount of β scission.

Rate Constants. We present some rate constants for quenching of benzophenone and substituted benzophenones in Table III. The results for *cis*-2-butene and isobutylene, as oxetane-forming olefins, are strikingly different from those for *trans*-dichloroethylene. The rate constants for *trans*-dichloroethylene (DCE) increase with increasing ketone triplet energy in the manner expected for an excitation-transfer process. We have previously[32] demonstrated excitation transfer as the mechanism of this isomerization through the use of secondary deuterium isotope effects. The rate constants for the butenes increase *in the opposite direction.* Further, while the DCE rate constants are reasonable, given $E_T \sim 72$ kcal/mol,[43] the butene rate constants ($E_T \sim 80$ kcal mol expected) are much too high for excitation transfer.

Clearly, the interaction in the butene cases is distinct from the excitation transfer process. The rate of excitation transfer otherwise should decrease markedly as ketone triplet energy decreases, just as for DCE. Accordingly, whatever fraction of the 2-butene isomerization is excitation transfer in the most favorable case (4,4′-dimethoxybenzophenone, with the highest E_T) the fraction must surely be much smaller in the others. The relative constancy of the isomerization quantum yields thus speaks against excitation transfer in all but the dimethoxy case. Further, in this case a decrease of only a factor of 6 for *cis*-2-butene relative to *trans*-DCE is observed. The decrease of excitation transfer rate is expected to be considerably greater than this on the basis of the triplet energy difference;[43,44] accordingly, we believe that even the dimethoxy case does not include excitation transfer as a major isomerization component. Isotope effect data (*vide infra*) further support the unimportance of excitation transfer.

Ruling out excitation transfer as a contributor to the interaction leaves biradical formation as the most plausible choice for chemically significant interaction of benzophenone triplets with the butenes. We must ask whether the butene rate data are consistent with the direct biradical mechanism, the excited state complex mechanism, or both.

Increase of rate constant with increasing ketone electronegativity is clearly consistent with the complex mechanism, if the complex has significant charge-transfer (CT) character. We would thus identify X in eq 2a–2c more precisely as having significant contribution from the following resonance form. Such complexes are by now well documented for amines.[22,45–49]

The ionization potentials of primary amines (*ca.* 8.7 eV) are lower than for the butenes (*ca.* 9.2 eV).[50] It is

---

(41) R. A. Caldwell and R. P. Gajewski, *J. Amer. Chem. Soc.*, **93**, 532 (1971).

(42) D. Valentine, Jr., and G. S. Hammond, *ibid.*, **94**, 3449 (1972).

(43) Z. R. Grabowski and A. Bylina, *Trans. Faraday Soc.*, **60**, 1131 (1964).

(44) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(45) S. G. Cohen, N. Stein, and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 521 (1968).

(46) R. S. Davidson and P. F. Lambeth, *Chem. Commun.*, 1265 (1967); 511 (1968); 1098 (1969).

(47) S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 2125 (1969).

(48) R. A. Caldwell, *ibid.*, 2121 (1969).

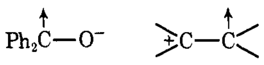
(49) L. A. Singer, *ibid.*, 923 (1969).

(50) D. W. Turner, *Advan. Phys. Org. Chem.*, **4**, 31 (1966).

Table III. Rate Constants for Quenching of Aromatic Ketone Triplets. Quantum Yields of *cis*-2-Butene Isomerization

Sensitizer	E_T[a]	$\phi_{c\rightarrow t}$ (*cis*-2-Butene)	k_Q, M^{-1} sec^{-1}	k_Q, M^{-1} sec^{-1} (*trans*-Dichloroethylene)	k_Q, M^{-1} sec^{-1} (Isobutylene)
4,4′-Dimethoxybenzophenone	69.4	0.35	4×10^6 [b]	2.4×10^7 [c]	1.1×10^7 [d]
Benzophenone	68.6	0.30	7×10^7 [b]	1.3×10^7 [e]	3×10^7 [d]
4-Trifluoromethylbenzophenone	67.6	0.34	2.2×10^8 [b]	6×10^6 [c]	7×10^7 [d]
4-Benzoylpyridine	67.1	0.34	3.3×10^8 [b]		

[a] D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968). [b] In benzene, 3660 Å excitation, relative to isoprene as quencher for which k_Q is assumed to be 5×10^9 M^{-1} sec^{-1} in all cases. Monitored by production of *trans*-2-butene. [c] In benzene, 3660 Å excitation, relative to *trans*-stilbene as quencher for which k_Q is assumed to be 5×10^9 M^{-1} sec^{-1} in all cases. Monitored by production of *cis*-dichloroethylene. [d] In benzene, 3660 Å excitation, relative to the stated values for *trans*-dichloroethylene. Monitored by production of *cis*-dichloroethylene. [e] In benzene, 3660 Å excitation, relative to isoprene as quencher for which k_Q is assumed to be 5×10^9 M^{-1} sec^{-1}.



gratifying to note that 2-butylamine quenches benzophenone triplet by a CT mechanism in benzene with a rate constant of 1.6×10^8 M^{-1} sec^{-1}, even faster than the 2-butene quenching rate.[51]

However, the biradical mechanism cannot be ruled out by kinetics alone. Although we have previously pointed out[32] that rate constants in the range of 10^7 M^{-1} sec^{-1} are exceedingly fast for direct biradical formation, based on alkoxy radical additions to olefins as a model, they are not inconceivably fast. Thus thiyl radicals show rate constants of this magnitude in olefin additions.[52]

The biradical mechanism is also not distinguishable from the complex mechanism *via* the substituent effect on rate constant. Note that eq 2 is, in effect, a one-electron reduction of the benzophenone triplet chromophore. Accordingly, the following equations suggest a suitable approach to substituent effects on photochemical abstraction of 1,4-biradical addition reactions of ketones.

	Substituent effect
(a) $\mathrm{Ar_2C{=}O} \xrightarrow{\text{excitation}} \mathrm{Ar_2CO^3}$	$\Delta E_T/\Delta\sigma = 1.6$ kcal
(b) $\mathrm{Ar_2C{=}O + H^+ + e^- \longrightarrow Ar_2\dot{C}{-}OH}$	$\Delta E_{1/2}/\Delta\sigma = 0.15$ V
(c) $\mathrm{Ar_2CO^3 + H^+ + e^- \longrightarrow Ar_2\dot{C}{-}OH}$	$\Delta E/\Delta\sigma = ?$

The expected similarity of substituent effects on the stability of **1** and of the ketyl radical in (b) above makes the Hammett ρ value for eq c, which in principle is available from those for a and b, relevant. The work of Zuman[53] on polarographic reduction of benzophenones in acidic medium shows a linear Hammett plot with slope 0.15 V, or about 3.5 kcal/mol. Substituent effects on triplet excitation energy from the work of Arnold[5] similarly show a linear Hammett plot with slope only about 1.6 kcal/mol. Precise comparison is difficult since the electrochemical work[53] was perforce done in protic medium (46% ethanol) and the photochemical work was done in hydrocarbon medium. Nonetheless, we doubt that substituent effects on the interactions of either ground or excited state ketone or ketyl radical with solvent will be large enough to vitiate the conclusion that, of the two reactions above, reduction is the more sensitive to substituent. Therefore reaction 2, even if elementary, should exhibit a positive Hammett ρ value.

The comparison of *cis*-2-butene and isobutylene as quenchers for a given ketone triplet is slightly more suggestive but no more conclusive. Using radical addition as a model, one would expect that isobutylene would be the more reactive. Addition in isobutylene can occur at an unsubstituted olefinic position to give a tertiary radical, while for 2-butene addition must occur at a more hindered secondary position and will only give a secondary radical. In two of the three cases, isobutylene is *less* reactive than *cis*-2-butene. This agrees better with the complex mechanism, since photoionization studies show *cis*-2-butene to have the lower ionization potential by about 0.1V.[54] *cis*-2-Butene should thus be a better CT donor. However, two predictive successes out of three are unimpressive, particularly since the reactivity differences are only factors of 2 or 3.

In summary, we regard distinctions between CT acceptor behavior and alkoxy radical behavior of ketone triplets as impossible to infer rigorously from our substituent effects. We note, however, the general trend observed by Wagner[30] of increasing quenching rate for triplet butyrophenone with decreasing olefin ionization potential, as suggestive of a CT complex intermediate.

Summary of Nonisotopic Experiments. Without recourse to the isotope effects we present later, no rigorous distinction between the biradical and complex mechanisms appears possible. The quantum yield inefficiency with 2-butene is suggestive of the complex mechanism, but not conclusive. We note the recent work of Stephenson,[55] which raises some fundamental questions about the nature of 1,4 biradicals. In particular, the slowness of spin inversion and fragmentation rates relative to bond-rotation rates no longer appears established. If spin inversion and β scission are comparable to the rate of rotation around the single bond indicated below, the sum, $\phi_{t\rightarrow c} + \phi_{c\rightarrow t} + \phi_{\text{oxetane}}$, measures no longer the total yield of biradical but merely approximates the yield of freely rotating biradicals.

The inconclusive nature of these conventional ex-

(51) S. G. Cohen and N. Stein, *J. Amer. Chem. Soc.*, **91**, 3690 (1969). We have recalculated their rate data assuming k_q for naphthalene to be 5×10^9 M^{-1} sec^{-1}.

(52) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 222, and references.

(53) P. Zuman, O. Exner, R. F. Rekker, and W. Nanta, *Collect. Czech. Chem. Commun.*, **33**, 3213 (1968).

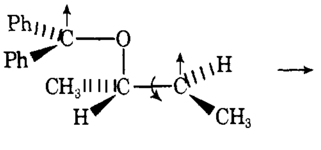
(54) D. A. Demeo and M. A. El-Sayed, *J. Chem. Phys.*, **52**, 2622 (1970). This paper includes some other data for isomeric 1,1-disubstituted *vs.* 1,2-disubstituted ethylenes. The latter appears to have the lower ionization potential in other cases also.

(55) (a) L. M. Stephenson and T. A. Gibson, *J. Amer. Chem. Soc.*, **94**, 4599 (1972); (b) L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, *ibid.*, **93**, 1984 (1971); (c) L. M. Stephenson and J. I. Brauman, *ibid.*, **93**, 1988 (1971).

Table IV. Isotope Effects in Cis–Trans Isomerization of 2-Butene and 3-Methyl-2-pentene Sensitized by Benzophenone[a]

Starting olefin	% isomerization	Reactant H/D	Product H/D	Product isotope effect
cis-2-Butene-*2,2-d*$_2$	20	1.014 ± 0.005[d]	1.024 ± 0.010[d]	1.010 ± 0.011[d]
	8	1.016 ± 0.006[d]	1.045 ± 0.005[d]	1.028 ± 0.009[d]
	12	0.994 ± 0.005[d]	1.018 ± 0.005[d]	1.024 ± 0.007[d]
trans-2-Butene-*2-d*$_1$	2	1.00 ± 0.01	0.984 ± 0.01	0.984 ± 0.015
	10	1.240 ± 0.01	1.220 ± 0.01	0.985 ± 0.015
cis-3-Methyl-2-pentene-*2-d*[b]	10	0.850 ± 0.003	0.848 ± 0.003	0.998 ± 0.004
	7.4	0.850 ± 0.002	0.855 ± 0.003[c]	1.006 ± 0.004
trans-3-Methyl-2-pentene-*2-d*[b]	6	0.981 ± 0.006	0.984 ± 0.004[c]	1.003 ± 0.007
	7.5	0.982 ± 0.003	0.991 ± 0.004[c]	1.011 ± 0.005

[a] Pyrex filter. [b] In 3-mm tubes of neat liquid. Benzophenone *ca.* 0.15 *M*. [c] Corrected for 0.2% of isomeric contaminant in the starting material. [d] For two deuteriums, measured in each case as *m/e* 56/58.



$$Ph_2C{=}O + trans\text{-}CH_3CH{=}CHCH_3 \quad (5)$$

periments makes a comparison of both the biradical and the complex mechanism with our isotope effect results worthwhile.

Isotope Effects. We have obtained two different kinds of isotope effect, providing different information. The isotope effect on initial quenching (IQIE) of ketone triplet may be obtained simply from the relative Stern–Volmer slopes in the quenching of some reaction of that triplet by labeled and unlabeled olefin, *viz.*, eq 6H and 6D.

$$Ph_2C{=}O^3 + \text{olefin-H} \longrightarrow \text{quenching} \quad (6H)$$

$$Ph_2C{=}O^3 + \text{olefin-D} \longrightarrow \text{quenching} \quad (6D)$$

Most of our data, however, relate to product isotope effects, in which a product is isolated and the position and extent of deuteration are established and compared with that of starting material. In the absence of reversibility (an assumption which may be examined), interpretation of such data follows analogously to that described in detail for triplet excitation transfer.[56] The product isotope effect (PIE) is not simply the IQIE but the IQIE multiplied by the isotope effects on partitioning of any intermediates. The comparison of IQIE and PIE results in the same system can thus be most informative in a comparison of postulated mechanisms. Product isotope effect is defined quantitatively as follows.

$$\text{PIE} \equiv \frac{(\text{unlabeled product})}{(\text{labeled product})} \bigg/ \frac{(\text{unlabeled reactant})}{(\text{labeled reactant})}$$

Isotope Effects in Olefin Isomerization. Table IV presents PIE data for cis–trans isomerization of several olefins. These effects are very small. In no case is the deviation from unity greater than 0.015/deuterium. As we have pointed out before,[32] excitation transfer as a mechanism for olefin isomerization is expected to introduce a large direct PIE. Thus, for cis–trans isomerization of 1,2-dichloroethylene sensitized by benzophenone, PIE's of 1.15 (cis → trans) and 1.18 (trans → cis) were observed.[32] The considerable difference between these values and those in Table IV clearly points out that the isomerization mechanisms differ. Since excitation transfer also fails to account adequately for the rate consants and the substituent effects in Table III, it cannot be important in these systems.

The biradical mechanism, by analogy to ground-state reactions, is expected to show an inverse isotope effect (at least for the IQIE). Possible origins of this effect have been discussed at length,[57,58] and there also is a considerable body of observed inverse isotope effects in radical additions to olefins.[57,59] We ourselves have reported an inverse isotope effect of 0.96 in the iodine catalyzed isomerization of β-methylstyrene-β-d[56] (though that appears not to be a simple radical addition[60]). We were initially concerned that the large rate constants (Table III) might preclude the observation of an isotope effect. However, the comparably fast addition of hydrogen atoms to simple alkenes does show a significant secondary deuterium isotope effect.[61]

If the biradical mechanism is correct the small and generally direct isotope effects in Table IV would present an anomaly. Whether the anomaly is real, or whether it resides in the inapplicability of IQIE expectations to a PIE experiment, will be discussed in the next section. We note, for now, that the complex mechanism merely requires that the olefin remain planar in the complex (*i.e.*, that little or no hybridization change occur) to be easily reconcilable with Table IV.

Isotope Effects in the Formation of 2 and 3. We have measured PIE's in the formation of oxetane from both *cis*-2-butene-*2,3-d*$_2$ and *trans*-2-butene-*2-d*. In the former case, competition between unlabeled and dilabeled alkene represents an *intermolecular* competition. Information about the preferred position of deuterium in an *intramolecular* competition arises from the latter experiment. Experimental detemination of the position and extent of label in **2** + **3** (treated as a mixture) affords information about biradical **6** and its mechanism of formation.

In Table V we present the results of both the intermolecular and intramolecular competitions. We have measured isotopic content primarily by the mass spectral fragmentation of the **2** + **3** mixture (in which **2** predominates), having checked the results in some instances by nmr (see Experimental Section). The *m/e*

---

[56] R. A. Caldwell, G. W. Sovocool, and R. J. Peresie, *J. Amer. Chem. Soc.*, **95**, 1496 (1973).

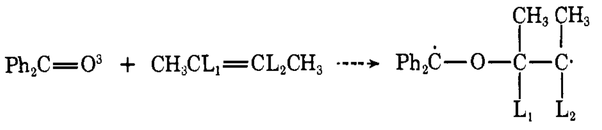
[57] E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

[58] A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, **80**, 2326 (1958).

[59] (a) D. B. Denney and N. Tunkel, *Chem. Ind.* (*London*), 1383 (1959); (b) M. Matsuoka and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 1261 (1961); (c) T. J. Katz and R. Dessau, *ibid.*, **85**, 2173 (1963); (d) S-H. Dai and W. R. Dolbier, Jr., *ibid.*, **94**, 3946, 3953 (1972).

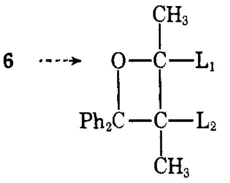
[60] (a) D. S. Trifan and P. D. Bartlett, *ibid.*, **81**, 5573 (1959); (b) G. Fraenkel and P. D. Bartlett, *ibid.*, **81**, 5582 (1959).

[61] M. Takahasi and R. J. Cvetanović, *Can. J. Chem.*, **40**, 1037 (1962).



$$Ph_2C{=}O^3 + CH_3CL_1{=}CL_2CH_3 \dashrightarrow Ph_2\dot{C}-O-\underset{L_1}{\overset{CH_3}{C}}-\underset{L_2}{\overset{CH_3}{C}}\cdot \quad (7)$$

6



(8)

2 + 3

Table V. Isotope Effects in Formation of 2,2-Diphenyl-3,4-dimethyloxetane[a]

2-Butene isomer	d_0	d_1	d_2	Oxetane m/e 194/195[b]	Δt, min
cis-2,3-d_2	1.016	0.064	(1.00)	1.058 ± 0.003	5
	1.016	0.064	(1.00)	1.047 ± 0.004	10
	1.016	0.064	(1.00)	1.011 ± 0.017	120
trans-2-d_1[c]	0.0082	(1.00)	<0.002	1.111 ± 0.002	10
	0.0082	(1.00)	<0.002	1.113 ± 0.005	17
	0.0082	(1.00)	<0.002	1.120 ± 0.005	24
	0.0082	(1.00)	<0.002	1.142 ± 0.004	60
	0.0082	(1.00)	<0.002	1.162 ± 0.005	122
	0.0082	(1.00)	<0.002	1.151 ± 0.005	415
	0.0082	(1.00)	<0.002	1.223 ± 0.008	320

[a] Pyrex filter. [b] Corrected for ^{13}C contribution. See text for determination of isotope effects. [c] Containing 10% cis isomer of the same isotopic composition.

194/195 ratio is the ratio of L_2-unlabeled to L_2-deuterated oxetane in each case, and conversion of these results to the position and extent of label in the oxetane mixture (primarily trans) involves at most a straightforward small correction for the minor isotopic constituents (monolabeled material in the d_0–d_2 mixture and unlabeled material in the d_1 compound).

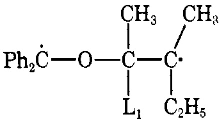
In both cases, a trend appears toward the preferential diminution of L_1-unlabeled oxetane as the time of irradiation increases. Since this position, being α to an oxygen, possesses a readily abstracted hydrogen, we suspect that such a secondary reaction of oxetane product occurs. We have no evidence to support this, but only a very small extent of such a secondary reaction would be required to introduce a few per cent change in the label ratio if a normal primary isotope effect of 4–6 or so occurred. The correct isotopic content or distribution in the initially formed oxetane is the value at low conversion. Within experimental error, the results became constant below 20 min irradiation time at m/e 194/195 = 1.05$_3$ for the intermolecular and 1.11$_2$ for the intramolecular competition (*cf.* Table V).

After correction for the minor isotopic constituents, the former result indicates a PIE of 1.03 ± 0.01 for intramolecular discrimination between unlabeled *cis*-2-butene and *cis*-2-butene-*2,3*-d_2 in formation of **2** + **3**. We compare the value of 1.02 ± 0.01 for isomerization of the same reactant mixture to trans. Clearly, there is no detectable isotopic discrimination in the reactions of biradical **6**, even though the $sp^3 \rightarrow sp^2$ change at L_1 in the fragmentation predicts a substantial direct isotope effect for this reaction of **6** and the $sp^2 \rightarrow sp^3$ change at L_2 in oxetane formation predicts an inverse isotope effect in that case. Interpreting this behavior on the basis of the Hammond postulate,[62] we conclude that the biradical **6** is extremely reactive and that these two reactions likely occur with little or no energy barrier. Considering calculations of the potential energy surface for tetramethylene,[63] we suggest that this may be a general result for 1,4 biradicals. Most importantly, since isotope effects on both products from **6** are direct, we now can conclude that *biradical* **6** *is formed with a small direct isotope effect, in clear contrast to expectations based on the biradical mechanism.* The conclusion reached in the previous section now can be stated more firmly. If the biradical is formed directly, a definite anomaly exists in the isotope effect; none exists if the complex mechanism operates.

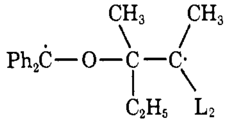
Examination of the intramolecular competition with monolabeled *trans*-2-butene reveals yet another anomaly. From Table V we calculate the ratio of **2** + **3**, L_1 = D, L_2 = H to **2** + **3**, L_1 = H, L_2 = D to be 1.10 ± 0.01. The small difference between this value and the m/e 194:195 ratio of 1.11$_2$ arises from the correction for d_0. Importantly, the absence of isotopic discrimination in the reactions of **6**, $L_1 = L_2$ = D, allows us to infer that the isotopic distribution in monolabeled **2** + **3** measures the isotopic distribution in monolabeled **6**. The monolabeled 2-butene results thus signify that **6**, L_1 = D, L_2 = H, is formed in preference to **6**, L_1 = H, L_2 = D, by the same factor of 1.10.

This observation is not easily reconcilable with the results of the intermolecular competition if the direct biradical formation mechanism operates. Even if one did accept a small direct isotope effect for the direct addition to *cis*-2-butene-*2,3*-d_2 rather than the well-precedented[57,59,61] inverse one, the inverse isotope effect for *trans*-2-butene-*2*-d_1, favoring **6**, L_1 = D, L_2 = H, would represent a clear internal contradiction.

Recent reports for some ground-state (2 + 2) cycloadditions[64,65] indicate the possibility of an inverse isotope effect at one vinyl position but a substantial direct isotope effect at the other. Although these results are thought now[64] to arise from the constraints of concertedness in these reactions (a manifest impossibility in our system, based on the stereochemical results), we believed it appropriate to try to test whether the resolution of the dichotomy might reside in such a balance, *i.e.*, an inverse isotope effect at L_1 opposing a slightly greater direct isotope effect at L_2. Although such a possibility seemed unlikely, we attempted to test it utilizing 3-methyl-2-pentene-*2*-d_1. In this case, two isomeric biradicals **7** and **8** are possible.



7



8

In **7**, the hydrogen or deuterium would be at an L_1-type position; in **8**, an L_2-type position. The "most

---

(62) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

(63) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *ibid.*, **92**, 7091 (1970).

(64) (a) J. E. Baldwin and J. A. Kapecki, *ibid.*, **91**, 3106 (1969); **92**, 4874 (1970); (b) J. E. Baldwin and J. A. Kapecki, *ibid.*, **92**, 4868 (1970).

(65) E. Koerner von Gustorf, D. V. White, J. Leitich, and D. Henneberg, *Tetrahedron Lett.*, 3113 (1969).

stable biradical" theory would predict a preference for **7** over **8** on the basis of the tertiary *vs.* secondary terminal. Accordingly, a net inverse isotope effect could be expected for the olefin isomerization. The results in Table IV show a zero or slightly direct isotope effect. While the uncertainty of the "most stable biradical" line of reasoning prevents a firm conclusion, we offer the results as tentative vitiation of the opposing isotope effect hypothesis.

Both the intramolecular competition and the 3-methyl-2-pentene results are easily rationalized in terms of the complex mechanism. Clearly, the hybridization change in collapse of the complex can introduce an inverse isotope effect; preference for **6**, L_1 = D, L_2 = H, over **6**, L_1 = H, L_2 = D, is quite sensible. Further, if the vinyl positions in the complex are not chemically distinct (except by virtue of olefin substituents), the expectation is that the (monolabeled) intermolecular isotope effect in 3-methyl-2-pentene-*2-d* should be roughly the square root of the (dilabeled) intermolecular isotope effect in *cis*-2-butene-*2,3-d*$_2$. The data are consistent with this expectation, though experimental uncertainties in these very small isotope effects preclude a strong statement. The isomerization of *trans*-2-butene-*2-d*$_1$ was the first experiment done,[66] and those results are sufficiently imprecise to render so careful a comparison impossible in that case.

Isotope Effects in the Interaction with Isobutylene. We have prepared isobutylene-β,β-d_2 to check the effect of vinyl deuteration in a different reaction in an effort to confirm our previous mechanistic findings. The results in Tables VI and VII are also consistent with the complex mechanism but are difficult to explain with the direct biradical mechanism.

Table VI. Isotope Effects in Total Quenching by Isobutylene-β,β-d_2 of Benzophenone. Sensitized Trans–Cis Isomerization of 1,2-Dichloroethylene

Isobutylene, mmol[c]		*trans*-$C_2H_2Cl_2$, mmol		$\phi_{cis\text{-}C_2H_2Cl_2}$[d]		
h_2	d_2	h_2	d_2	h_2	d_2	k_{QH}/k_{QD}[e]
0	0	2.05		0.512		
0.91[a]	0.91[a]	9.05	9.05	0.380	0.374	0.943 (±15%)
1.12[a]	1.13[a]	5.65	5.65	0.337	0.322	0.875 (±13%)
1.13[a]	1.16[a]	2.88	2.88	0.263	0.254	0.963 (±7%)
1.12[a]	1.12[a]	1.70	1.70	0.200	0.204	1.032 (±5%)
1.11[b]	1.13[b]	3.07	3.07	0.258	0.258	1.017 (±6%)
1.11[b]	1.12[b]	2.05	2.05	0.214	0.210	0.980 (±5%)
1.13[b]	1.13[b]	1.53	1.53	0.181	0.175	0.969 (±4%)

[a] Purified by successive distillations only. [b] Purified by preparative gc on BC/SN. [c] Error ±1%. Total solution volume 3.2 ml. [d] Error in gc analyses ±1% as measured by repetitive injections. Cumulative errors in quantum yield are ±2%. [e] Error estimates based on errors in $\phi_{cis\text{-}C_2H_2Cl_2}$.

Table VII. Product Isotope Effect in the Formation of 2,2-Diphenyl-3,3-dimethyloxetane from Isobutylene-β,β-d_2 in Neat Isobutylene

% conversion of Ph_2CO	Isobutylene reactant H_2/D_2 (nmr)	Isobutylene reactant H_2/D_2 (ms)	Oxetane product H_2/D_2 (nmr)	PIE[c]
22	1.010 ± 0.006	1.014 ± 0.005	0.847 ± 0.013	0.842
67	0.974 ± 0.008	1.012 ± 0.002	0.867 ± 0.013	0.862
67	0.974 ± 0.008	1.012 ± 0.002	0.898 ± 0.006[a]	0.893
67	0.974 ± 0.008	1.012 ± 0.002	0.887 ± 0.009[b]	0.882
80	1.010 ± 0.008	1.020 ± 0.004	0.908 ± 0.008	0.903[a]

[a] Chromatographed and recrystallized from hexane. [b] Rechromatographed and recrystallized from hexane. [c] Defined as H_2/D_2 oxetane ratio ÷ 1.006, the average value of H_2/D_2 for isobutylene reactant. Experiments were done consecutively as listed, with the recovered isobutylene from one run becoming the reactant for the next. Nmr analyses of the vinyl protons presume precisely 6.00 hydrogens in the methyl resonance, and their constancy thus indicates no detectable scrambling of deuterium within isobutylene during the reaction. [d] In benzene solvent (isobutylene 0.5 *M*).

The IQIE was measured by isobutylene quenching of dichloroethylene isomerization (Table VI). Utmost precision was required. The high concentrations necessary for accurate volumetric measurements of isobutylene unfortunately resulted in a slight but detectable curvature in a Stern–Volmer plot. Either of the two quenching rate constants or the decay ratio of the dichloroethylene triplet could be slightly affected by the considerable changes in medium represented by the solute concentration extremes, with concomitant curvature. We decided to treat the data as a series of two-point Stern–Volmer plots. Each row across in Table VI represents a matched pair of experiments with nearly the same concentration of all components; one (h_2) has unlabeled isobutylene and the other (d_2) dilabeled (98%) isobutylene. The assumption that replacement of the unlabeled with the labeled component makes no change in any parameter (except for the isotope effect on the isobutylene quenching rate constant) seems the safest assumption that we could possibly make. The small differences in actual concentration between the h_2 and d_2 components of the matched pair should surely introduce no detectable medium effects on any rate constant. Accordingly, eq 9 may be used to calculate the IQIE for quenching

$$\frac{k_{QH}}{k_{QD}} \equiv \text{IQIE} = \frac{((\phi_0/\phi) - 1)_{h2}}{((\phi_0/\phi) - 1)_{d2}} \frac{(C_4H_6D_2)}{(C_4H_8)} \times \frac{(C_2H_2Cl_2 \text{ in } h_2)}{(C_2H_2Cl_2 \text{ in } d_2)} \quad (9)$$

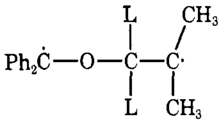
of benzophenone triplets by isobutylene in each matched pair.

The value determined for k_{QH}/k_{QD} by a weighted least-squares averaging procedure is 0.986 ± 0.036, or 0.993 ± 0.018 per deuterium. The value is not useful in an absolute sense, since it is intermediate between and within experimental error of both the expected value for a direct biradical mechanism and the values we observed above for 2-butene and 3-methyl-2-pentene quenching. However, a comparison with the PIE observed for oxetane **4** (the major reaction product) is most revealing.

The results in Table VII demonstrate a value for the PIE for formation of **4** that is significantly lower than the IQIE. The PIE is 0.87 ± 0.02 (0.935 ± 0.01/D) for the runs in neat isobutylene, though possibly slightly higher in benzene solvent. The direct biradical mechanism could only be reconciled with this difference if there were an isotope effect on the subsequent partitioning of **9**, the biradical precursor of **4**. The yield of **5** is low (*ca.* 8% of the yield of **4**). Its precursor, **10**, presumably is also formed with low probability and thus should have an insignificant effect on the IQIE and the PIE for **4**.

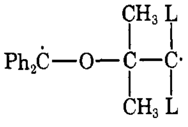
---

(66) S. P. James, B.S. Honors Thesis, Cornell University, 1969.



$\mathrm{Ph_2\dot{C}{-}O{-}CL_2{-}\dot{C}(CH_3)_2}$

9



$\mathrm{Ph_2\dot{C}{-}O{-}C(CH_3)_2{-}\dot{C}L_2}$

10

A substantially faster fragmentation of **9**,L = H, relative to **9**,L = D, would be analogous to the ground-state isotope effects seen in $sp^3 \rightarrow sp^2$ situations and would reconcile the direct biradical mechanism with the IQIE and PIE; however, it would then be at odds with the absence of discrimination in the reactions of dideuterated **6**.

Reconciliation with the complex mechanism, on the other hand, is easy. The same inverse isotope effect seen in the selective formation of **6**, L_1 = D, L_2 = H, from 2-butene-*2-d* would be expected in the collapse of a complex leading to **9**. Since formation of **10** is probably not significant, the process competing with collapse to **9** is most likely decay of the complex to ground state, eq 2c. The low quantum yield of **4** (Table II) is consistent with this. The IQIE near unity is also consistent with the 2-butene results.

Nature of the Complex. We believe that our results require intermediacy of the complex prior to biradical formation in the previously accepted n,π^* triplet ketone–olefin photocycloaddition mechanism. We examine the data to summarize the inferences that can be drawn about the complex, its mode of formation, and its reactivity.

First the noninverse IQIE's and the divergence of IQIE and PIE results for both 2-butene-*2-d*$_1$ and isobutylene-β,β-d_2 clearly suggest *irreversible* complex formation. A prior equilibrium would require both PIE's and IQIE's to reflect the $sp^2 \rightarrow sp^3$ hybridization change. Taylor and Hammond[21] have suggested irreversible complex formation in the quenching of naphthalene singlets by piperylene on basis of secondary deuterium isotope effects. However, excited state complex formation from stilbene singlets and tetramethylethylene is clearly reversible.[23] Our scanty knowledge of excited-state complexes does not yet allow prediction of when irreversible formation may be expected. Efforts to elucidate this point would be profitable.

The observation of isotope effects on the collapse of the complex in the two systems we have presented indicates that significant selectivity between its possible modes of reaction may be expected. Obviously, the lifetime of the complex is finite, though we could only guess at a value. Further experiments to attempt interception of these (and other) excited state complexes may yield fascinating new photoreactions. Chandross and Thomas[67] have seen termolecular interactions in solute quenching of some singlet exciplex fluoroescences.

The rate differences in Table III are not large. Hammett ρ values of less than unity are indicated; the 2-butene rate constants do not fit a Hammett relationship well. By comparison, converting the polarographic data[53] (for complete one-electron transfer) to "powers-of-ten" units gives a Hammett ρ of +2.5. Were the polarographic data taken in hydrocarbon solvent, with its lower polarity, the ρ value should have been considerably greater. We thus believe that, though the direction of the rate constants indicates significant change transfer nature to the complex, change transfer is surely not complete at the transition state (and of course not necessarily complete in the complex itself). Kochevar and Wagner[30] similarly found that the effect of olefin structure on its rate constant for quenching butyrophenone triplets in "energy units" ($\Delta E = 2.3RT\ \Delta \log k$) was about a tenth of the effect on its ionization potential.

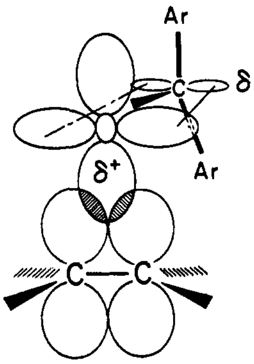


Figure 1. A structural hypothesis for the complex.

Another point of interest in the complex mechanism is the implied inapplicability of the simple "most stable biradical" hypothesis.[14] The direction of collapse of the complex (which we presume does not itself distinguish the olefinic carbons) is dependent on factors in addition to biradical stability. For example, charge distributions and polarizabilities in the complex might be involved. While more data must be gathered before the relative importances may be assessed, including relative rates of fragmentation *vs.* cyclization of isomeric biradicals such as **7** and **8**, or **9** and **10**, we no longer see divergence of product distributions from "most stable biradical" predictions as anomalous at all.

There is very little we can say with certainty about the structure of the complex. Turro has shown for diaryl ketones that quenching by electron-rich olefins occurs in the carbonyl plane, *i.e.*, that the n orbital is involved.[68] The importance of n,π^* states in oxetane formation from diaryl ketones[5] of course similarly suggests n-orbital involvement. A possible structure which would include n-orbital participation, a geometry symmetric with respect to the olefin double bond, and which would maintain geometric integrity of the olefin, is shown in Figure 1.

Acknowledgment is made to the donors of the Petroleum Research Fund (Grant 3031-A4), administered by the American Chemical Society, and the National Science Foundation (Grants No. GP-14796 and No. GP-30717) for financial support.

---

(67) E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, **9**, 397 (1971).

(68) N. J. Turro, J. C. Dalton, G. Farrington, M. Niemczyk, and D. M. Pond, *J. Amer. Chem. Soc.*, **92**, 6978 (1970).