for the ratio $k_r/k_d$. It is tempting to postulate that energy transfer takes place to an upper vibrational level of I so as to allow a vertical Franck–Condon transition to the excited triplet state. Since the diene system of I is twisted,[3,4] flattening of the molecule corresponds to an increase in the ground-state potential energy. The nmr spectrum of I indicates that the $\alpha$-hydrogens are equivalent at room temperature; *i.e.*, ring flipping is rapid on the nmr time scale at room temperature. The efficiency of energy transfer would be related to the population of the vibrational levels only if decay of sensitizer triplets competes with energy transfer to vibrationally excited ground states of I. Clearly, much more data are necessary to establish whether such an effect can operate in this or other systems. An alternative possibility is that low-energy triplet sensitizers are inducing reaction by a Schenck mechanism[19] involving initial bond formation to I. Such a mechanism has been invoked for sensitized olefin isomerization induced by donors with lowest $n,\pi^*$ triplet states.[20]

Since the earlier publication,[4] a preliminary value for the quantum yield of the direct photodecarbonylation of I has been measured at 313 nm and found to be 0.31 for disappearance of I. Since intersystem crossing from the excited singlet is clearly unimportant,[4] the inefficiency of the reaction must be attributed either to rapid radiationless decay of the singlet or to reversible formation of an intermediate formed by $\alpha$ cleavage on one side of the double bond.[21,22] Decarbonylation might proceed from such a diradical intermediate, in competition with return to starting material I, or might be the result of a concerted reaction of the excited singlet which competes with $\alpha$ cleavage. Further experiments are necessary to decide between these alternatives. It is certain, however, that all pathways for singlet-state deactivation and reaction are much faster than intersystem crossing to the triplet,[4] although this does not appear to be the case with some unsaturated ketones of comparable symmetry.[23]

### Experimental Section

**Materials.**—*cis,cis*-3,5-Cycloheptadienone was prepared as described previously.[4] Solvents, reagents, and sensitizers were purified by distillation or recrystallization before use.

**Photolysis Procedure.**—Photolyses of I at room temperature, sensitized and unsensitized, were carried out as described previously.[4] Photolyses at liquid nitrogen ($-196°$) temperatures were carried out in a Pyrex tube immersed in liquid nitrogen in a large dewar attached at one end to a quartz glass tube. The dewar was placed inside a Rayonet reactor and irradiated with 3650-Å lamps for 4.5 hr. Photolyses at $-70°$ were carried out by immersing a Hanovia immersion cell containing a 450-W high-pressure mercury lamp in a large dewar containing Dry Ice and ethanol. There was an insulating air space around the immersion well provided by a large reaction cell so that water could be circulated within the immersion well without freezing. Samples were in solution in Pyrex tubes surrounding the immersion well outside the insulation but within the dewar. Typical runs involved 40–60 mg of dienone I in 35 ml of ether containing

enough sensitizer to absorb $>99\%$ of the incident light. In some runs, Corning 7380 filters were placed between the lamp and the sample tube to restrict the incident light to $>340$ nm. The progress of the reaction was followed by glpc analysis[4] on a 4-ft column of 5% SE-30 silicone on Chromosorb G.

For the controlled-temperature irradiations between 0 and $-70°$, the degassed solutions of I, sensitizer, and internal standard were sealed in a 3- or 4-mm Pyrex tube, which was irradiated externally with a Hanovia 450-W lamp inside a Pyrex immersion well through a Corning 7380 filter. The temperature within the tube was maintained using the cooling apparatus for the esr spectrometer, in which a stream of nitrogen at a set temperature was passed around the outside of the sample tube. The heat exchanger for the cooling gas was a Dry Ice–acetone bath. Experiments at lower temperatures with a liquid nitrogen bath for cooling the gas were less reproducible. Analysis by glpc was carried out as above.

**Quantum yields** for disappearance of I were determined as described earlier,[24] using a Bausch and Lomb high-intensity grating monochromator and ferrioxalate actinometry.

**Registry No.**—I, 25090-28-2; III, 25090-29-3.

(24) D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **90**, 5145 (1968).

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# Photochemical Rearrangements of $\alpha$-Benzyloxystyrenes to $\beta$-Phenylpropiophenones

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*Contribution 118 from the Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan*

There are a number of examples of photochemical rearrangements of aryl ethers, *e.g.*, the rearrangements of aryl phenyl ethers to arylphenols,[1a,b] that of phenoxycarboxylic acids to hydroxyphenylcarboxylic acids,[2] and that of allyl phenyl ether to allylphenol.[3] They may be initiated by homolytic fission of phenoxycarbon bonds in electronically excited ether molecules, since phenol is detected in the products. Among them, the photochemical rearrangement of allyl phenyl ether, or Claisen rearrangement, is important since it can be discussed in view of the orbital symmetry.[4]

The rearrangement of $\alpha$-benzyloxystyrene to $\beta$-phenylpropionphenone catalyzed by azobisisobutyronitrile (AIBN) has been known to be intermolecular radical-chain reaction, where $\cdot CH_2Ph$ acts as a chain carrier.[5a] The rearrangement also occurs on heating at *ca.* 200° in the absence of AIBN. In this case, orbital symmetry arguments may suggest that the shift of 1,3-benzyl radical with continuous overlap is not

(1) (a) D. P. Kelly and J. T. Pinhey, *Tetrahedron Lett.*, 5933 (1966); (b) H.-I. Joschek and S. I. Miller, *J. Amer. Chem. Soc.*, **88**, 3269 (1966).

(2) D. P. Kelly and J. T. Pinhey, *Tetrahedron Lett.*, 3427 (1964).

(3) (a) M. S. Kharasch, G. Stampa, and W. Nudenberg, *Science*, **116**, 309 (1952); (b) G. Koga, N. Kikuchi, and N. Koga, *Bull. Chem. Soc. Jap.*, **41**, 745 (1968).

(4) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965); (b) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(5) (a) K. B. Wiberg, R. R. Kintner, and E. L. Motell, *J. Amer. Chem. Soc.*, **85**, 450 (1963). (b) It was observed that **1a** was stable but **1c** was rearranged partially to the corresponding photo ketone (**2c**) in a glpc column.

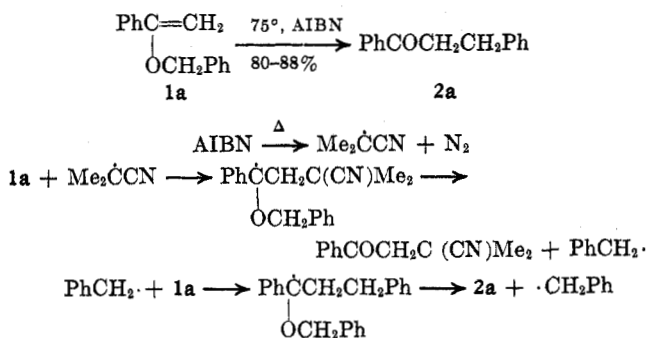(19) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belg.*, **71**, 781 (1962).

(20) N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **91**, 3265 (1969); J. Saltiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3658 (1969).

(21) P. J. Wagner and R. W. Spoerke, *ibid.*, **91**, 4437 (1969).
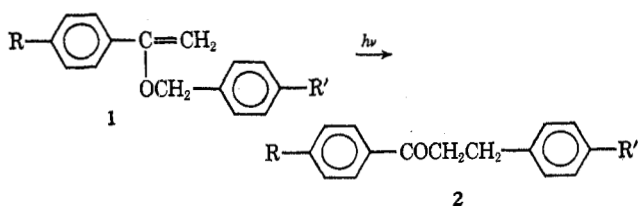
(22) In the earlier paper, it was explicitly stated that the results did not exclude a two-step nonconcerted decarbonylation mechanism; see especially footnote 34 in ref 4.

(23) P. S. Engel and H. Ziffer, *Tetrahedron Lett.*, **59**, 5181 (1969).

feasible. This means the intermolecular nature of the thermal rearrangement.

$$\underset{\underset{\substack{|\\ \text{OCH}_2\text{Ph}\\ \textbf{1a}}}{\text{PhC}=\text{CH}_2}}{} \xrightarrow[\text{80-88\%}]{75^\circ,\ \text{AIBN}} \underset{\textbf{2a}}{\text{PhCOCH}_2\text{CH}_2\text{Ph}}$$

$$\text{AIBN} \xrightarrow{\Delta} \text{Me}_2\dot{\text{C}}\text{CN} + \text{N}_2$$

$$\textbf{1a} + \text{Me}_2\dot{\text{C}}\text{CN} \longrightarrow \underset{\underset{\text{OCH}_2\text{Ph}}{|}}{\text{Ph}\dot{\text{C}}\text{CH}_2\text{C}(\text{CN})\text{Me}_2} \longrightarrow$$

$$\text{PhCOCH}_2\text{C (CN)Me}_2 + \text{PhCH}_2\cdot$$

$$\text{PhCH}_2\cdot + \textbf{1a} \longrightarrow \underset{\underset{\text{OCH}_2\text{Ph}}{|}}{\text{Ph}\dot{\text{C}}\text{CH}_2\text{CH}_2\text{Ph}} \longrightarrow \textbf{2a} + \cdot\text{CH}_2\text{Ph}$$

In contrast, if the similar rearrangement occurs photochemically, the orbital symmetry arguments suggest that the 1,3-benzyl shift should be feasible and hence the rearrangement is intramolecular. In fact, the rearrangement of **1a** easily occurs on uv irradiation in *n*-hexane at room temperature, resulting in a high yield (91%) of **2a**.

$$\text{R}-\hspace{-4pt}\underset{\underset{\text{OCH}_2\text{--}\!\langle\!\bigcirc\!\rangle\!\text{--R}'}{|}}{\langle\!\bigcirc\!\rangle}\hspace{-4pt}\overset{\text{C}=\text{CH}_2}{} \xrightarrow{h\nu}$$

**1**

$$\text{R}-\langle\!\bigcirc\!\rangle\text{--COCH}_2\text{CH}_2\text{--}\langle\!\bigcirc\!\rangle\text{--R}'$$

**2**

a, R, R' = H
b, R = H; R' = Me
c, R = Me; R' = Me
d, R = Cl; R' = H
e, R = MeO; R' = H

The present paper describes results of our study on the nature of this photorearrangement including the effects of a heavy atom solvent and various substituents to discuss a probable mechanism.

A *n*-hexane solution of 0.32 m*M* of α-benzyloxystyrene (**1a**) was irradiated in a sealed quartz cell. The uv spectra at intervals of 30 min are shown in Figure 1. After 1.5 hr irradiation the spectrum becomes identical with that of authentic β-phenylpropiophenone (**2a**), and the yield was estimated uv spectrophotometrically to be 91%. Passing oxygen through the solution before irradiation gave lower yield (35%) of **2a**, while passing oxygen during irradiation gave no photo ketone but an autoxidation product, benzoic acid.

This rearrangement was further confirmed by the following experiments. For the isolation of the photo ketone, a *n*-hexane solution of **1a** (1 g) was irradiated at 28° for 11 hr, N₂ gas being bubbled into the mixture during irradiation. After irradiation, the reaction mixture was chromatographed on silicic acid column to isolate the photo ketone (0.2 g) which was identified as **2a** by direct comparison of mp 69.5–70.0° (lit.[5a] 70.0–71.0°) and uv and ir spectra with the authentic sample. The lower yield on the preparative scale might be caused by deposit of photoproducts on the wall of the reaction vessel during irradiation.

The quantum yields for the formation of photo ketones are listed in Table I. Accuracy is within ±0.01. The order of reactivity by these *para* substituents in styrene residue is Me > H > MeO > Cl, although the substituent effect is small. The effect of *p*-methyl group in benzyl residue is negligibly small.
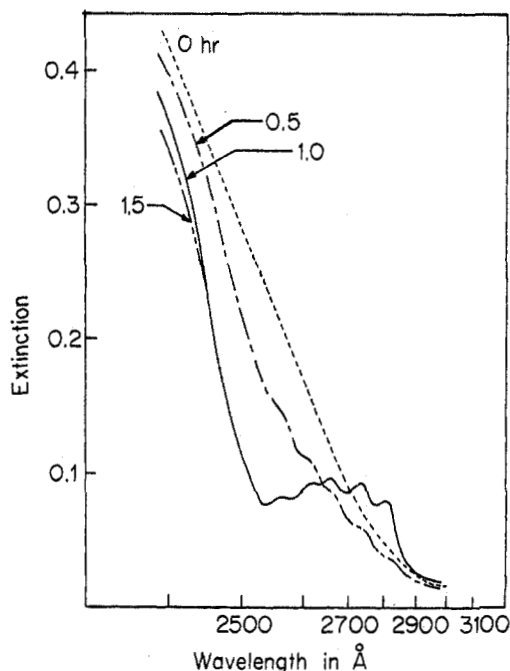


Figure 1.—Absorption spectra for **1a** in *n*-hexane as a function of irradiation time (hr) at 25–28°.

TABLE I

QUANTUM YIELDS, $\phi$, FOR THE FORMATION OF PHOTO KETONES (2) IN *n*-HEXANE AT 20–23°

| Compd | R | R' | $\phi$ |
|---|---|---|---|
| **2a** | H | H | 0.11 |
| **2b** | H | Me | 0.12 |
| **2c** | Me | Me | 0.15 |
| **2d** | Cl | H | 0.04 |
| **2e** | MeO | H | 0.07 |

For the estimation of intramolecularity of rearrangement, an equimolar mixture of **1a** ($\phi$ = 0.11) and **1c**[5b] ($\phi$ = 0.15) was irradiated in *n*-hexane, the product being chromatographed on a silicic acid column to isolate photo ketones. The resulting mixture of photo ketones was then subjected to glpc analysis. Thus 92% intramolecularity was observed for the rearrangement by comparing the areas of peaks. The results of crossed reaction indicate that an intramolecular mechanism is predominating as has been observed in other photochemical rearrangements such as the rearrangements of aryl esters[6] and sulfonamides.[7]

The absorption spectra of **1** are relatively simple and $\lambda_{max}$ in 2470–2610 Å are shown in Table II. The irradiation with 2400–2700 Å light probably populates the $\pi,\pi^*$ states of **1**. As described above, the rearrangement is quenched by oxygen. Hence, it seems likely that a triplet state rather than a singlet state is involved in the rearrangement in spite of the low efficiency of intersystem crossing of most conjugated olefins.[8] An increase of quantum yield for the formation of **2a** to 0.47 in *n*-propyl chloride as a heavy atom solvent confirms the above conclusion. The result

(6) (a) V. I. Stenberg, "Organic Photochemistry," O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 127; (b) D. V. Rao and V. Lambert, *J. Org. Chem.*, **32**, 2896 (1967); (c) M. R. Sandner and D. J. Trecker, *J. Amer. Chem. Soc.*, **89**, 5725 (1967).

(7) H. Nozaki, S. Okada, Y. Noyori, and S. Kawanishi, *Tetrahedron*, **22**, 2177 (1966).

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

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF
1 AND 2 IN n-HEXANE

| Compd | $\lambda_{max}$, Å (log $\epsilon$) | Compd | $\lambda_{max}$, Å (log $\epsilon$) |
|---|---|---|---|
| 1a | 2470 (3.75) | 2a | 2392 (4.22), 2650 (2.89), 2685 (2.94), 2790 (2.94), 2870 (2.82), 3240 (1.78) |
| 1b | 2470 (3.84) | 2b | 2370 (3.87), 2656 (2.98), 2685 (2.99), 2744 (3.02), 2875 (2.71), 3260 (1.84) |
| 1c | 2500 (3.50) | 2c | 2755 (3.12), 2890 (2.70), 3210 (1.99) |
| 1d | 2490 (4.01) | 2d | 2515 (4.19), 2740 (2.94), 2873 (2.60), 3250 (1.79) |
| 1e | 2610 (4.13) | 2e | 2650 (4.18), 2770 (4.00), 3180 (2.06) |

may be explained by assuming an increased yield of intersystem crossing, $\phi_{ST}$, by the heavy atom.[9]
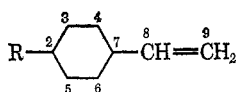


Calculations of the electron densities in the lowest excited states originating from $\pi,\pi^*$ transitions of *para*-substituted styrenes in place of 1 were performed by means of HMO method using the values of $a$, $l$, and $\lambda$ reported by Hatano, Tamura, and Kambara.[10] The electron densities at 8 and 9 positions are summarized in Table III. As shown in Table III, it seems that

TABLE III

ELECTRON DENSITIES AT 8 AND 9 POSITIONS
IN THE LOWEST EXCITED *para*-SUBSTITUTED STYRENES



| R | Electron density | |
| | $C_8$ | $C_9$ |
|---|---|---|
| H | 0.3105 | 0.5095 |
| Me | 0.2109 | 0.5139 |
| Cl | 0.2213 | 0.5346 |
| MeO | 0.1077 | 0.3244 |

the quantum yield, $\phi$, depends on the electron density in the lowest excited state at the 9 position except in 1d. The lower yield of 2d may be explained by assuming a shorter lifetime of the triplet state of 1d by the presence of a halogen atom.[11]

As described above, the orbital symmetry arguments suggest that the 1,3-benzyl shift, that is, a sigmatropic reaction of order [1,3], should be feasible photochemically, and hence the photochemical rearrangement should be intramolecular. However, our results on the crossed reaction indicated the presence of 8% crossover products. This could be explained by a nonconcerted reaction involving competition between cage

recombination and diffusion out of the solvent cage. Therefore, the mechanism may be as follows.
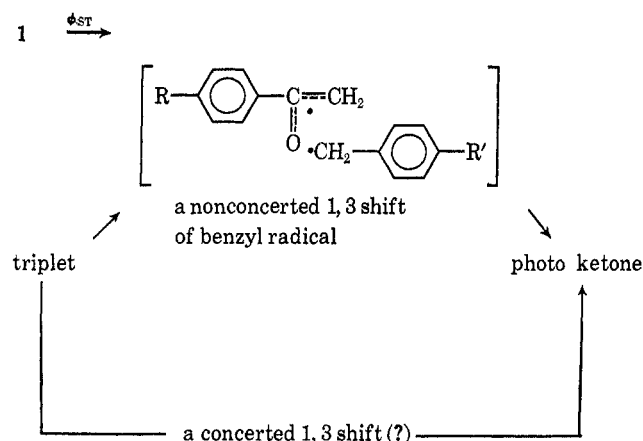
### Experimental Section

**Materials.**—α-Benzyloxystyrene (1a) was prepared from styrene and benzyl alcohol according to the known procedure,[5a] bp 133–134° (2 mm), $n^{25}D$ 1.5835 (lit.[5a] 1.5850). Authentic β-phenylpropiophenone (2a) was prepared by azobisisobutyronitrile (AIBN) catalyzed rearrangement[5a] of 1a followed by duplicate recrystallizations from n-hexane, mp 70.0–70.5° (lit.[5a] 70.0–71.0°). α-p-Methylbenzyloxy-p-methylstyrene (1c), bp 156–159° (1 mm), was similarly prepared from p-methylstyrene, bp 66.0–66.5° (22 mm), and p-methylbenzyl alcohol, mp 60° (lit.[12] 61°), which was obtained by direct hydrolysis of ω-bromo-p-xylene in the presence of an emulsifier. Authentic β-p-tolylethyl p-tolyl ketone (2c) was prepared by the similar catalytic rearrangement of 1c followed by recrystallization from n-hexane, mp 65.0–65.5°.

*Anal.* Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.10; H, 7.61.

p-Tolyl β-phenylethyl ketone (2f) was prepared by Grignard synthesis from p-bromotoluene and cinnamaldehyde,[13] mp 68.5–69.0° (lit.[13] 69°).

Other substituted benzyloxystyrenes were similarly prepared from substituted styrenes and benzyl alcohols. They were identified by means of ir and uv spectra and melting points of the corresponding ketones obtained by their AIBN-catalyzed rearrangements: α-p-methylbenzyloxystyrene (1b), bp 150–154° (1 mm), β-p-tolylpropiophenone (2b), its oxime, mp 84–85° (lit.[13] 85–86°), α-benzyloxy-p-chlorostyrene (1d), bp 166–168° (2.5 mm), p-chlorophenyl β-phenylethyl ketone (2d), mp 77.8–78.3° (lit.[13] 78°), α-benzyloxy-p-methoxystyrene (1e), bp 148–151° (2.5 mm), p-anisyl β-phenylethyl ketone (2e), mp 96.0–96.2° (lit.[14] 97°).

n-Hexane (first grade) was passed through a silica gel column followed by distillation, bp 67.5–68.0°. n-Propyl chloride was prepared by the reaction of n-propyl alcohol with concentrated hydrogen chloride,[15] bp 44–45°.

The ir spectra were measured by a Perkin-Elmer Model 337 grating instrument and uv spectra were recorded by a Shimadzu type SV-50A spectrophotometer. A Yanagimoto Model GCG-220 gas chromatograph was used for glpc.

**Irradiation of 1a.**—A solution of 0.32 m*M* 1a in n-hexane was placed in a quartz square cell (path length 1 cm), and it was sealed after bubbling a slow stream of dry $N_2$ through the mixture. A Halos 30W low-pressure Hg lamp, which emits almost exclusively 2537-Å light, was used as a light source. The cell was placed at the distance of 25 cm from the light source and irradiation was carried out at 32–35°. The uv spectra of the reaction mixture were recorded at intervals of 30 min for 1.5 hr.

**Isolation of 2a.**—A solution of 1a (1 g) in n-hexane (400 ml) was placed in a reaction vessel equipped with a $N_2$ gas inlet, a

(9) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 57.

(10) M. Hatano, N. Tamura, and S. Kambara, *Kogyo Kagaku Zasshi*, 70, 2016 (1967).

(11) D. S. McClure, *J. Chem. Phys.*, 17, 905 (1949).

(12) D. Davidson and M. Weiss, "Organic Syntheses," Coll. Vol. II, Wiley, New York, N. Y., 1948, p 590.

(13) H. Burton and C. K. Ingold, *J. Chem. Soc.*, 904 (1928).

(14) P. Pfeiffer and P. A. Negreanu, *Ber.*, 50, 1465 (1917).

(15) J. E. Copenhaver and A. M. Whaley, "Organic Syntheses," Coll. Vol. I, Wiley, New York, N. Y., 1946, p 142.

thermometer, and a condenser. The Halos 30W low-pressure Hg lamp was immersed in the reaction mixture. The solution was irradiated under $N_2$ at 28° for 11 hr. After irradiation, the reaction mixture was carefully condensed and introduced into a silicic acid column (diam 1 cm, height 20 cm) for chromatography. Elution with n-hexane gave **2a** (0.2 g) and elution with a mixed solvent of 50% ethanol and 50% n-hexane gave unreacted **1a** (0.5 g).

**Crossed Reaction of 1a and 1c.**—A solution of **1a** (1.1 g) and **1c** (1.2 g) in n-hexane (800 ml) was irradiated similarly at 28–35° for 54 hr. The irradiated solution was carefully condensed and chromatographed on silicic acid column. Elution with n-hexane gave a mixture of photo ketones. Analysis of the mixture was done by means of glpc, employing a Yanagimoto Model GCG-220 operated with a 1 × 4 mm column packed with 10% PEG 20M on 40–60 mesh Fire Brick C-22 with a He flow of 60 ml/min at 241°. The similarity of the retention times of the peaks of authentic materials with those of the samples established their identity.

**Determination of Quantum Yields for Formation of Photo Ketones.**—The quantum yields were determined by means of a liquid phase chemical actinometer using potassium ferrioxalate at 20–23°. A Halos 30W low-pressure Hg lamp without filter was used as a light source, and produced photo ketones were determined by uv spectrophotometry. A general procedure is as follows. A solution of 0.1–0.2 m*M* **1a** in n-hexane was placed in a square quartz cell (path length 1 cm), and it was sealed under $N_2$ atmosphere. A solution of 6 m*M* potassium ferrioxalate in 0.1 *N* $H_2SO_4$ was placed in an actinometer cell (path length 5 cm). Irradiation was started by opening a shutter and continued for 1 hr. The number of molecules of produced **2a** in a cell was determined spectrophotometrically. The light intensity absorbed by the reactant was determined by the procedure reported by Parker and Hatchard.[16] The quantum yield was calculated from these data.

**Registry No.**—**1a**, 25109-98-2; **1b**, 25186-49-6; **1c**, 25186-50-9; **1d**, 25186-51-0; **1e**, 25150-08-7; **2a**, 1083-30-3; **2b**, 1669-50-7; **2c**, 20615-46-7; **2d**, 5739-37-7; **2e**, 5739-38-8.

(16) (a) C. A. Parker, *Proc. Roy. Soc., Ser. A*, **220**, 104 (1953); (b) C. G. Hatchard and C. A. Parker, *ibid.*, **235**, 518 (1956).

# A Facile Synthesis of Methanesulfonate Esters

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Reactive sulfonate esters are especially useful because of their synthetic versatility and ability to initiate carbonium ion reactions. The usual Tipson procedure[4] is not suited for the synthesis of reactive sulfonate esters owing to facile alkylation of the solvent, pyridine, by the products.[5] For the synthesis of propargyl brosylates and tosylates, this side reaction has been suppressed by the use of excess 2,6-lutidine in methylene chloride solution,[6] and, in the case of benzyl tosylates, by reaction of tosyl chloride with the appropriate lithium[7] or sodium[5] alkoxide. Although very reactive species may be prepared by these procedures, the relatively long reaction times (days) of the former and the strongly basic conditions of the latter seem to limit both procedures to products which are stable to elimination. Another successful procedure for the preparation of reactive tosylates is reaction of the corresponding alkyl iodide with silver tosylate.[8] Both benzyl and branched chain tosylates may be prepared by this method; however, the stereochemistry of the product is uncertain. Recently Coates and Chen have published a synthesis of reactive tosylates which involves oxidation of the corresponding sulfinates with m-chloroperbenzoic acid in methylene chloride solution.[9] This method appears to have general applicability, although, from the corresponding alcohol, two synthetic steps are required. The method also seems to be restricted to molecules not containing easily oxidized functionality.

For some time we have synthesized methanesulfonate esters (mesylates) from the corresponding alcohols using a procedure based on the mechanistic studies of Truce.[10] We wish to report the experimental details of this procedure which is extraordinarily simple and rapid and appears to be of diverse applicability. Table I lists some of the mesylates prepared by this procedure. Repetitive integration of the 60-MHz ¹H nmr spectra showed that in each case the product was over 95% esterified. No by-products were observed. Our procedure deviates from the usual Tipson procedure[4] by the use of triethylamine as base and methylene chloride as solvent. In the light of recent evidence[11] it is apparent that the mechanistic course of the reaction has been changed from the usual nucleophilic addition of the alcohol to the sulfonyl group to addition of the alcohol to the sulfene[12] derived from mesyl chloride by E2 elimination of hydrogen chloride.[11] The facile esterification of a number of tertiary and neopentyl systems (Table I) indicates that the reagent has a small steric requirement. The nucleophilicity of the alcohol is unimportant as shown by the ready esterification of 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoro-2-propanol. Furthermore, conditions are sufficiently mild that even very reactive systems such as 1-methylcyclobutyl[13] and α-phenethyl may be esterified. Indeed, in our experience, all alcohols are esterified by this procedure; the limiting factor seems to be the stability of the product.[14]

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(2) Taken in part from the Ph.D. dissertation of R. K. C., University of Southern Calfornia, 1969; Stauffer Chemical Company Fellow, 1966; National Science Foundation Summer Trainee, 1967–1968; Petroleum Research Fund Fellow, 1968. We are grateful for this financial aid and support.

(3) Department of Chemistry, University of Southern California; Alfred P. Sloan Fellow, 1969–1971.

(4) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(5) J. K. Kochi and G. S. Hammond, *J. Amer. Chem. Soc.*, **75**, 3443 (1953).

(6) Private communication of unpublished results from Mr. William Dowd, Department of Chemistry, Indiana University.

(7) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Sheppele, *J. Amer. Chem. Soc.*, **89**, 370 (1967).

(8) H. M. R. Hoffman, *J. Chem. Soc.*, 6748 (1965).

(9) R. M. Coates and J. P. Chen, *Tetrahedron Lett.*, 2705 (1969).

(10) W. E. Truce and J. R. Norell, *J. Amer. Chem. Soc.*, **85**, 3231 (1963).

(11) J. F. King and T. W. S. Lee, *ibid.*, **91**, 6524 (1969).

(12) For leading references to sulfenes as reaction intermediates, see G. Opitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967).

(13) This mesylate has been prepared previously in methylene chloride solution using pyridine as base: A. Majerski, M. Nikoletic, S. Borcic, and D. E. Sunko, *Tetrahedron*, **23**, 661 (1967).

(14) Those systems which decompose under the reaction conditions give the corresponding olefins. For example, with 2.5 molar equiv of amine, attempted esterification of 2-(3,5-ditrifluoromethylphenyl)-2-propanol gave α-methyl-3,5-ditrifluoromethylstyrene in 73% yield.