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.

Acknowledgment.—The authors wish to thank Dr. Y. Sawaki for his gifts of *p*-methylstyrene and *p*-chlorostyrene.

(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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Received March 11, 1970

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).

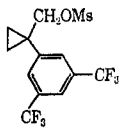
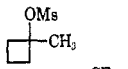
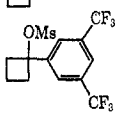
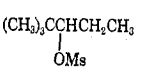
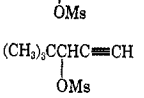
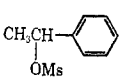
(11) J. F. King and T. W. S. Lee, *ibid.*, **91**, 6524 (1969).

(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.

TABLE I
SOME MESYLATES PREPARED USING TRIETHYLAMINE AS BASE IN METHYLENE CHLORIDE SOLUTION

Compd[a]	No.	Yield, %[b]	Physical properties[c]
	1	95	Mp 70–71[d,e]
	2		Highly reactive liquid which decomposes slowly at 0°[e]
	3	92	Mp 48.5–49° dec[d,e]
Adamantyl-1-OMs	4	82[g]	Mp 46–48° dec
	5	90	Colorless liquid[f]
	6	92	Colorless liquid[f,h]
	7		Highly reactive liquid which decomposes violently at room temperature
CF_3CH_2OMs	8	87[i]	Colorless liquid, bp 97–99° (35 mm)
$(CF_3)_2CHOMs$	9	85[i]	Colorless liquid, bp 157–158°

[a] All mesylates were characterized by their 60-MHz ^1H nmr spectra. [b] Corresponds to weight of product obtained after removal of solvent and pumping the residue down to 1 mm at 0° for 4 hr. [c] Melting point and boiling point data are uncorrected. [d] See ref 16 for preparation and characterization of the precursor alcohol. [e] Purity was further confirmed by titrimetric rate analysis of solvolysis and infinity titer (see ref 16). [f] Purity was further confirmed by conductometric rate analysis of solvolysis. [g] Yield after recrystallization from hexane. [h] Precursor alcohol and mesylate were prepared by Mr. William Dowd, Department of Chemistry, Indiana University. [i] Yield after fractional distillation.

We have found mesylates to be quite useful as synthetic intermediates. They are about three times *less* reactive toward solvolysis than the corresponding tosylates.[15] With suitably unhindered systems, mesylate is easily displaced by nucleophiles such as halide or hydride.[16] In the latter case, where reduction is performed with excess lithium aluminum hydride in ether, mesylates are especially useful because the mesylate fragment reduces to methyl mercaptan, which is easily removed.

Experimental Section

General Procedure for the Preparation of Mesylates.—To an approximately 0.2 *M* solution of the alcohol in methylene[17] chloride solution containing a 50% molar excess of triethylamine at 0 to −10° was added a 10% excess of methanesulfonyl chloride (mesyl chloride) over a period of 5–10 min.[18] Stirring for an additional 10–15 min completed the reaction. The reaction mixture was transferred to a separatory funnel with the aid of more methylene chloride. The mixture was first extracted with ice water, followed by cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine. Drying of the methylene chloride solution followed by solvent removal gave the product,[19] which was pure enough for most uses including solvolysis.

Registry No.—**1**, 25236-57-1; **2**, 935-20-6; **3**, 25236-59-3; **4**, 25236-60-6; **5**, 25236-61-7; **6**, 25236-62-8; **7**, 25236-63-9; **8**, 25236-64-0; **9**, 25236-65-1.

Acknowledgment.—The latter stages of this research which were carried out at Indiana University were supported in part by Grant AT(11-1)-1008 from the U. S. Atomic Energy Commission (Document No. COO-1008-7).

(15) R. E. Robertson, *Progr. Phys. Org. Chem.*, **4**, 213 (1967).

(16) R. K. Crossland, Ph.D. Dissertation, University of Southern California, Los Angeles, Calif., 1970.

(17) Both cyclohexane and pentane may also be used as solvent. The choice is based solely on the solubility of the starting alcohol.

(18) Mesyl chloride was redistilled; triethylamine was refluxed over phthalic anhydride, distilled, and then redistilled from potassium hydroxide pellets; methylene chloride was taken from a freshly opened bottle of AR grade. Anhydrous reaction conditions were maintained.

(19) The more reactive the product mesylate, the more slowly the mesyl chloride was added and the lower the temperature. For very reactive systems the glassware used in the work-up was prechilled and the temperature of the mesylate was never allowed to exceed 0°. With large-scale preparations (~1 mol) the excess of triethylamine may be reduced to 20%.

Thermal Decomposition of Liquid *t*-Amyl Peroxide

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Decomposition of liquid *t*-butyl peroxide (I) at its boiling point (110°) in absence of any solvent proceeds at a rate approximately 2.8 times faster than expected from its unimolecular decomposition rate (reaction 1) in the gas phase.[2] Isobutylene oxide (II) is formed as a major decomposition product along with *t*-butyl alcohol and acetone (see Table I). The induced decomposition of I and formation of II along with the other products are explained in terms of a free-radical reaction including the chain sequence 3 and 4.[2]

$$\underset{\text{I}}{(CH_3)_3COOC(CH_3)_3} \longrightarrow 2(CH_3)_3CO\cdot \qquad (1)$$

$$(CH_3)_3CO\cdot + \text{I} \longrightarrow CH_3COCH_3 + CH_3\cdot \qquad (2)$$

$$(CH_3)_3CO\cdot \text{ (or } CH_3\cdot) + \text{I} \longrightarrow \underset{\text{(or } CH_4)}{(CH_3)_3COH} + \underset{\displaystyle CH_2\cdot}{(CH_3)_2COOC(CH_3)_3} \qquad (3)$$

$$\underset{\displaystyle CH_2\cdot}{(CH_3)_2COOC(CH_3)_3} \longrightarrow \underset{\displaystyle CH_2}{(CH_3)_2C\text{—}O} + \cdot OC(CH_3)_3 \qquad (4)$$

II

Reaction of *t*-amyl peroxide (III) by a similar route would involve abstraction of a secondary hydrogen as shown in reactions 8 and 10. The greater reactivity of secondary hydrogens relative to primary hydrogens toward abstraction would suggest that the chain sequence 8 and 10 could possibly be a more important route for the decomposition of III than it is for I. The products of the decomposition of III in the liquid phase

(1) Taken in part from the thesis submitted by K. J. J. in partial fulfillment of the requirements for the Ph.D. degree from the University of Kansas, 1969.

(2) J. H. Raley, F. F. Rust, and W. E. Vaughn, *J. Amer. Chem. Soc.*, **70**, 88 (1948); E. R. Bell, F. F. Rust, and W. E. Vaughn, *ibid.*, **72**, 337 (1950).