Syntheses of Halogenosulfuranes with a Five-Membered Ring Bonded to Sulfur via Oxygen and Nitrogen

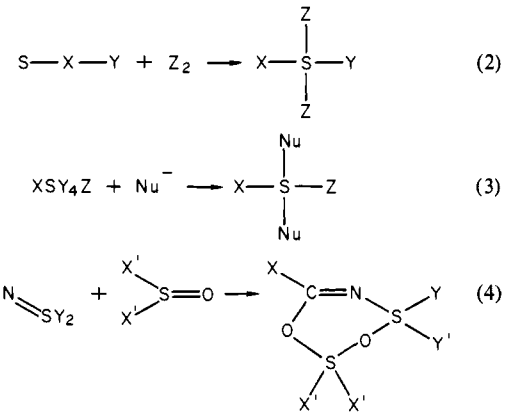
Kiyoshi Tanaka and Jean'ne M. Shreeve*

Contribution from the Department of Chemistry, University of Idaho, Moscow, Idaho 83843.
Received August 25, 1980

Abstract: The reactions of *o*-aminophenol and silylated *o*-aminophenol with (*F*-isopropyl)sulfur trifluoride afforded 2-(*F*-isopropyl)benzo-2-thioxazole **1**. The addition reactions of hydrogen halides with thioxazole **1** gave 2-halogeno-2-(*F*-isopropyl)benzo-2-thioxazoline **3** and their ion pairs **4** which are in equilibrium.

There has been considerable interest in tetracoordinate sulfur(IV) compounds (sulfuranes) over the years.[1] Sulfuranes have been synthesized via conversion of the functional groups on sulfur(IV) compounds (eq 1),[2] oxidative addition of sulfur(II) compounds (eq 2),[3] reductive elimination of sulfur(VI) compounds (eq 3),[4] and cycloaddition of dienic sulfur(IV) compounds (eq 4).[5] Another possible approach to sulfuranes is the addition reaction

$$X_3S{-}Y + Nu^- \rightarrow X_3S{-}Nu + Y^- \quad (1)$$

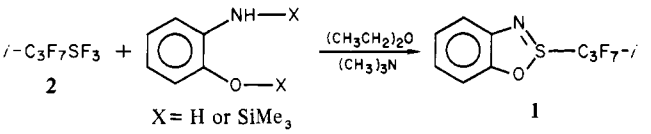


e.g., X, Y, Z = halogen or *F*-alkyl; X′ = alkyl or alkoxy

to a double bond including sulfur(IV). We now want to report preparation of a stable cyclic iminosulfur compound, 2-(*F*-isopropyl)benzo-2-thioxazole (**1**), by the reaction of (*F*-isopropyl)-sulfur trifluoride with *o*-aminophenol and the synthesis of halogenosulfuranes[6] with a five-membered ring bonded to sulfur via oxygen and nitrogen by the addition of hydrogen halides to the thioxazole **1**.

Results and Discussion

The reaction of (*F*-isopropyl)sulfur trifluoride **2** with *o*-aminophenol in diethyl ether in the presence of 3 equiv of trimethylamine gave thioxazole **1** in up to 83% yield. The yields



were not constant, with each reaction affording between 30% and 83% of **1**. A similar reaction of **2** with silylated *o*-aminophenol in the presence of sodium fluoride gave **1** in only 24% yield. Thioxazole **1** was identified by spectral measurements and elemental analysis. The mass spectrum shows a molecular peak at *m/e* 307 and the UV spectrum indicated a considerable band at λ 405 nm due to the sulfur–nitrogen double bond, which is almost identical with λ 410 nm due to the sulfur–nitrogen double bond in $C_6H_5N{=}S{=}NC_6H_5$.[7] Recrystallization of thioxazole **1** from pentane gave red plate crystals which are stable at room temperature for more than 2 weeks and are easily sublimed at 0.01 torr.

The reaction of thioxazole **1** with an excess of hydrogen chloride in dichloromethane at room temperature was so rapid that none of the adduct **3** was obtained. Only a salt was collected. Its infrared spectrum showed it to be an ammonium salt of unknown composition. However, the use of diethyl ether in place of dichloromethane retarded the reaction rate and resulted in the formation of the adduct **3**. Some unreacted starting material **1** remained. Thin-layer chromatography (silica gel, dichloromethane) of this adduct showed one spot at the place of R_f 0.32. This adduct was separated by column chromatography and recrystallized from pentane to give a compound with a sharp melting point, 81–82 °C. The mass spectrum of this adduct shows the molecular peaks at *m/e* 345 and 343 in appropriate ratio for chlorine isotopes, and elemental analysis indicates the formula $C_9H_5NF_7ClOS$. These results suggest that the adduct is derived from **1** and 1 equiv of hydrogen chloride. The ^{19}F NMR spectral data show the presence of two chemically different *F*-isopropyl groups. For the *F*-methyl groups, the chemical shift difference is only 0.027 ppm (2.5 Hz using the HA-100 NMR spectrometer operating at 94.1 MHz). This resonance is comprised of two well-defined overlapped doublets centered at ϕ −74.6 ($J_{CF_3\text{-}CF}$ = 10.8 Hz). The *F*-methine fluorine atoms are seen as two nearly superimposed septets centered at ϕ −165.92 and −166.04 with a chemical shift difference of 0.12 MHz (11.2 Hz at 94.1 MHz). Since $J_{CF\text{-}CF_3}$ = 10.8 Hz, which is nearly equal to the chemical shift difference, the spectrum is actually made up of eight rather broad peaks resulting from nearly perfect overlap at the center with less exact overlaps of the lower intensity peaks. The ^1H NMR spectrum reveals two broad peaks at δ 5.4 and 5.0. The infrared spectrum (KBr) gives two sharp absorption bands at 3530 and 3395 cm^{-1}. These data strongly support that one of the two

(1) (a) Musher, J. I. *Angew Chem., Int. Ed. Engl.* **1969**, *8*, 54. (b) In "Sulfur Research Trends"; Gould, R. F., Ed.; American Chemical Society: Washington, D.C., 1972; Vol. 110, 44–52. (c) Shreeve, J. M. *Isr. J. Chem.* **1978**, *17*, 1 and references therein. (d) Shreeve, J. M. In "Sulfur in Organic and Inorganic Chemistry", Vol. IV, 1982 in press and references therein.

(2) (a) Adzima, L. J.; Chiang, C. C.; Paul, I. C.; Martin, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 953. (b) Adzima, L. J.; Martin, J. C. *Ibid.* **1977**, *99*, 1657. (c) Darragh, J. I.; Hossain, S. F.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1975**, 218. (d) Sheppard, W. A. *J. Am. Chem. Soc.* **1971**, *93*, 5597. (e) Sprenger, G. H.; Cowley, A. H. *J. Fluorine Chem.* **1976**, *7*, 333. (f) Hodges, K. C.; Schomburg, D.; Weiss, J. V.; Schmutzler, R. *J. Am. Chem. Soc.* **1977**, *99*, 6096. (g) Sauer, D. T.; Shreeve, J. M. *J. Fluorine Chem.* **1971/72**, *1*, 1. (h) Mews, R.; Alange, G. G.; Glemser, O. *Naturwissenschaftaen* **1970**, *57*, 245. (i) Wilson, G. E., Jr.; Belkind, B. A. *J. Am. Chem. Soc.* **1978**, *100*, 8124. (j) Perozzi, E. F.; Martin, J. C. *Ibid.* **1979**, *101*, 1591.

(3) (a) Campbell, B. S.; Denney, D. B.; Denney, D. Z.; Shih, L. *J. Am. Chem. Soc.* **1975**, *97*, 3850. (b) Yagupolskii, Yu. L.; Savina T. I. *Zh. Org. Khim.* **1979**, *15*, 438; *Chem. Abstr.* **1979**, *90* 203618. (c) Gombler, W. *Z. Anorg. Allg. Chem.* **1978**, *439*, 193. (d) Kitazume, T.; Shreeve, J. M. J. *Am. Chem. Soc.* **1977**, *99*, 4194. (e) Ruppert, I. *Chem. Ber.* **1979**, *112*, 3023. (f) Mir, Q.-C.; Laurence, K. A.; Shreeve, R. W.; Babb, D. P.; Shreeve, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 5949.

(4) Kitazume, T.; Shreeve, J. M. *J. Fluorine Chem.* **1977**, *9*, 175.

(5) Kitazume, T.; Shreeve, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 985.

(6) Martin, J. C.; Balthazor, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 152 and references therein.

(7) Cramer, R. D. *J. Org. Chem.* **1961**, *26*, 3476.

0002-7863/81/1503-4067$01.25/0 © 1981 American Chemical Society

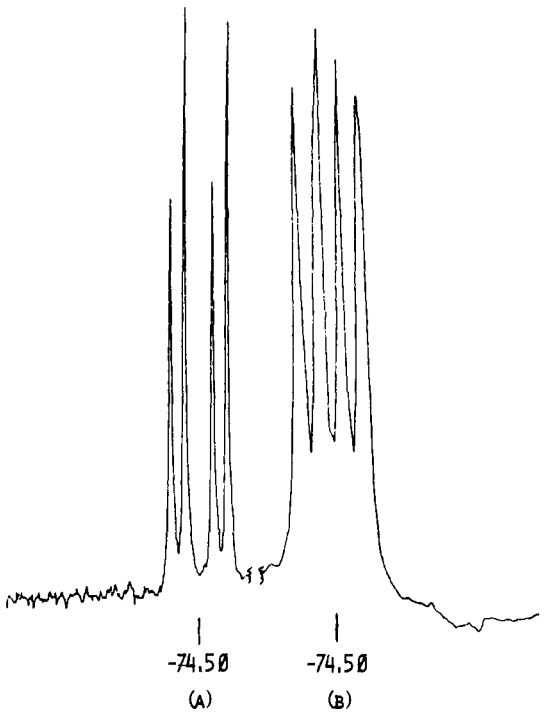
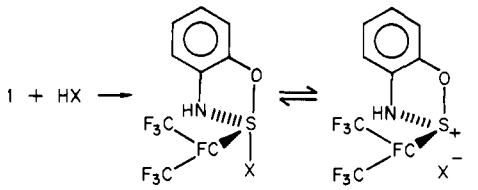
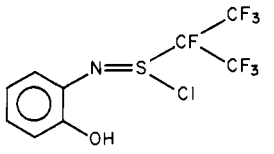


Figure 1. (A) ^{19}FNMR spectrum of **3b–4b** in $CDCl_3$. (B) ^{19}F NMR spectrum of **3b–4b** in $CDCl_3$ after additions of $(C_2H_5)_4NBr$.

compounds is 2-chloro-2-(*F*-isopropyl)benzo-2-thioxazoline (chlorosulfurane) (**3a**) and that the other compound is an isomer or tautomer of **3a**. At first, **5** seemed to be the most likely



structure of the tautomer. The band at 3530 cm^{-1} in the infrared spectrum could be assigned to the phenolic hydroxyl group. Moreover, additional support for **5** arose from the fact that the carbon analogues, benzoxazolines, and their tautomer (Schiff bases) are in equilibrium.[8] However, tautomer **5** is precluded



5

on the basis of the ultraviolet spectrum of **3** in which there is no absorption band around 410 nm which is the normal region of the N=S double bond. In **1**, the N=S absorption band is at 405 nm. The reaction of thioxazole **1** with hydrogen bromide proceeded smoothly in diethyl ether even at −78 °C to give the adduct as well as an ammonium salt. This adduct was similarly separated by column chromatography. Spectroscopic properties of this adduct indicate the same trend as with hydrogen chloride; i.e., this is a mixture consisting of the bromosulfurane **3b** and its isomer. A plausible structure of this isomer is ion pair **4b**. The ^{19}F NMR spectral data show two overlapping doublets centered at ϕ −74.5 with the chemical shift difference again being very small. These are assigned to two sets of CF_3 groups in two nonequivalent *F*-isopropyl groups (J_{CF_3-CF} = 10.7 Hz at 84.26 MHz for each doublet). The CF_3 region is shown in the Figure 1A. Two sets of septets are centered at ϕ −165.5. This is a mixture of the bromosulfurane **3b** and an isomer which may be the ion pair **4b**. Addition of excess tetraethyl ammonium bromide to the NMR tube containing the adduct in $CDCl_3$ produced a marked change in the relative intensities of the two doublets causing them to become about equal (Figure 1B). These results strongly support the argument that the isomer is the ion pair **4b** which is in equilibrium with the bromosulfurane **3b**. These differences are not, then, attributable to the effects arising from the presence of the chiral center in **3b**.

This is not surprising, since the electron-releasing effect of the nitrogen bonded to sulfur stabilizes the cationic charge on sulfur, and the relative stable ion pairs **4** are formed. Adducts **3** and **4** are easily sublimed at 0.01 torr and are stable at room temperature for more than 1 week.

In the synthesis of sulfuranes by addition to S=N double bonds, the stabilizing effect of a five-membered ring[9] is seen to be important because the similar addition of hydrogen chloride to *S,S*-bis(trifluoromethyl)sulfimide, $(CF_3)_2S$=NH, results in formation of ammonium chloride only.[10]

Experimental Section

All gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus equipped with a Heise-Bourdon tube gauge. All gaseous starting materials were measured quantitatively by PVT techniques. (*F*-Isopropyl)sulfur trifluoride (**2**) was prepared by the reaction of *F*-propene with sulfur tetrafluoride.[11] Silylated *o*-aminophenol was prepared by following the procedures described in the literature using bis(trimethylsilyl)acetamide.[12] Infrared spectra were recorded with a Perkin-Elmer 599B spectrometer. ^{19}F NMR spectra were obtained on either a Varian HA-100 or JEOL FX-90Q spectrometer by using CCl_3F as an internal standard. ^{1}H NMR spectra were measured on a Varian EM 360 with tetramethylsilane as an internal standard. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E spectrometer operating at 17 eV. Ultraviolet spectra were recorded with a Beckman ACTA MVII spectrophotometer. Elemental analyses were performed either in house or by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Reaction of (*F*-Isopropyl)sulfur Trifluoride (2) with *o*-Aminophenol. (*F*-Isopropyl)sulfur trifluoride (**2**) (12.0 mmol) and trimethylamine (36.0 mmol) were condensed into a 75-mL Hoke cylinder containing *o*-aminophenol (1.19 g, 10.9 mmol) and diethyl ether (10 mL) at −196 °C. The reaction mixture was warmed to room temperature and agitated for 12 h. After the ammonium salt was removed by dry filtration (silica gel, CH_2Cl_2), the residual thioxazole **1** was sublimed at 0.01 torr to give 2.78 g of thioxazole **1** (83% yield). Further purification was done by recrystallization from pentane (mp 57.5–58.5 °C); R_f 0.71 (silica gel, CH_2Cl_2); infrared spectrum (KBr) 1631 (m), 1593 (m), 1531 (vw), 1480 (w), 1421 (w), 1280 (vs), 1230 (vs), 1195 (sh), 1163 (m), 1130 (m), 967 (s), 941 (s), 913 (m), 864 (vw), 776 (w), 760 (sh), 744 (m), 722 (m), 685 (m), 598 (vw), 540 (w), 506 (vw), 410 (vw), 363 (w), 327 (vw) cm^{-1}; mass spectrum (*m/e*) M^+ 307, $[(CF_3)_2C{=}S]^+$ 182, $[C_6H_4NSO]^+$ 138, $(CF_3CS]^+$ 113, $[C_6H_4NO]^+$ 106; ^{19}F NMR ($CDCl_3$) ϕ −73.1 (6 F, d, J = 9.4 Hz), −170.6 (1 F, sept, J = 9.4 Hz); ^{1}H NMR ($CDCl_3$) δ 6.6–7.6 (arom); UV (hexane) λ 405 nm (log ϵ = 3.66), 345 (log ϵ = 401), 333 (shoulder, log ϵ = 3.82).

Anal. Calcd for $C_9H_4NF_7OS$: C, 35.20; H, 1.31; N, 4.56; F, 43.3. Found: C, 35.33; H, 1.40; N, 4.67; F, 43.2.

Reaction of (*F*-Isopropyl)sulfur Trifluoride (2) with Silylated *o*-Aminophenol. (*F*-Isopropyl)sulfur trifluoride (**2**) (3.3 mmol) was condensed into a 30-mL Hoke cylinder containing silylated *o*-aminophenol (760 mg, 3 mmol), anhydrous sodium fluoride (250 mg, 6 mmol), and anhydrous diethyl ether (2 mL) at −196 °C. The reaction mixture was warmed to room temperature and agitated for 12 h. The reaction mixture was treated as described above to give 220 mg of thioxazole **1** (24% yield).

Reaction of Thioxazole 1 with Hydrogen Chloride. To a 100-mL Pyrex glass vessel equipped with a Teflon stopcock and containing thioxazole (450 mg, 1.47 mmol) and diethyl ether (15 mL) was added hydrogen chloride (10.3 mmol) at −196 °C. This mixture was warmed to room

(8) Cornforth, J. W. In "Heterocyclic Compounds"; Elderfield, R. C., Ed.; Wiley: New York, 1957; Vol. 5 Chapters 5 and 6.

(9) Martin, J. C.; Perozzi, E. F. *J. Am. Chem. Soc.* **1974**, *96*, 3155.
(10) Kumar, R. C.; Shreeve, J. M., unpublished results.
(11) Rosenberg, R. M.; Muetterties, E. L. *Inorg. Chem.* **1962**, *1*, 756.
(12) Klebe, J. F.; Finkbeiner, H.; White, D. M. *J. Am. Chem. Soc.* **1966**, *88*, 3390.

temperature and was stirred for 1 day. Pumping off the volatile compound left the residual product of which ^{19}F NMR analysis showed 35% yield of adduct **3a** and **4a** (conversion yield is 77%) and starting material. Separation using column chromatography (silica gel, CH_2Cl_2) gave 100 mg of adduct **3a** and **4a** (20%). Purification was completed by recrystallization from pentane. Adduct **3a** and **4a**: mp 81–82 °C; R_f 0.32 (silica gel, CH_2Cl_2); infrared spectrum (KBr) 3530 (m), 3395 (m), 1600 (w), 1505 (s), 1443 (m), 1400 (w), 1285 (vs), 1270 (s), 1230 (vs), 1215 (vs), 1175 (m), 1165 (m), 1120 (m), 1090 (vw), 970 (m), 940 (w), 885 (w), 863 (vw), 848 (vw), 815 (vw), 760 (vw), 720 (w), 660 (vw), 587 (vw), 500 (vw), 410 (vw) cm^{-1}; mass spectrum (*m/e*) M^+ 345, 343, $[(CF_3)_2C{=}S]^+$ 182, $[M - C_3F_7]^+$ 176, 174, $[M - C_3F_7H_2]^+$ 174, 172, $[CF_3CFS]^+$ 132, $[CF_3CS]^+$ 113, $[CF_3]^+$ 69; ^{19}F NMR ($CDCl_3$) ϕ −74.6 (6 F, 2 d, both J = 10.8 Hz), −166.0 (1 F, 2 sept, both J = 10.8 Hz); ^1H NMR ($CDCl_3$) δ 7.4–6.7 (arom), 5.4 (br s), 5.0 (br s); UV (hexane) λ 292 nm (log ϵ = 3.67), 239 (log ϵ = 4.12).

Anal. Calcd for $C_9H_5NF_7ClOS$: C, 31.46; H, 1.47; N, 4.08. Found: C, 31.18; H, 1.48; N, 4.04.

Reaction of Thioxazole 1 with Hydrogen Bromide. To a 100-mL Pyrex glass vessel equipped with a Teflon stopcock and containing thioxazole **1** (300 mg, 0.98 mmol) and diethyl ether (2 mL) was added hydrogen bromide (6.86 mmol) at −196 °C. This mixture was stirred −78 °C for 1 h. After the volatile compound was pumped off, the precipitated ammonium salt was filtered off by using methylene chloride. The filtrate was evaporated to leave crude adduct **3b** and **4b**. This was purified by column chromatography (silica gel, CH_2Cl_2) to give 130 mg of adduct **3b** and **4b** (34%). Recrystallization from pentane afforded the pure adduct **3b** and **4b**: mp 94.5–96.5 °C; R_f 0.19 (silica gel, CH_2Cl_2); infrared spectrum (KBr) 3503 (m), 3383 (s), 1595 (m), 1496 (s), 1440 (s), 1395 (w), 1303 (vs), 1285 (vs), 1265 (vs), 1220 (vs), 1165 (s), 1118 (s), 1080 (vw), 970 (s), 938 (m), 868 (m), 847 (w), 815 (m), 761 (w), 723 (m), 642 (w), 583 (w), , 550 (vw), 410 (w), 385 (vw), 360 (vw) cm^{-1}; mass spectrum (*m/e*) M^+ 389, 387, $[M - CF_4H_2O]^+$, 283, 281, $[M - C_3F_7]^+$ 220, 218, $[M - H_2C_3F_7]^+$ 218, 216, $[C_6H_4SBr]^+$ 189, 187, $[C_6H_3SBr]^+$ 188, 186, $[(CF_3)_2CS]^+$ 182, $[CF_2(CF_3)CS]^+$ 163, $[CFSOBr]^+$ 160, 158, $[CFS(NH)Br]^+$ 159, 157, $[CF_3(F)CS]^+$ 132, $[CF_3CS]^+$ 113, $[CF_2CS]^+$ 94, $[CF_3]^+$ 69; ^{19}F NMR ($CDCl_3$) ϕ −74.5 (6 F, 2 d, both J = 10.7 Hz), −165.5 (1 F, 2 sept, both J = 13.3 Hz); ^1H NMR ($CDCl_3$) δ 7.6–6.9 (arom), 5.4 (br s).

Anal. Calcd for $C_9H_5NF_7BrOS$: C, 27.86, H, 1.30. Found: C, 28.04; H, 1.43.

Acknowledgment is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grant CHE-7727395) for support of this research. We thank Charles Barinaga and Dennis Gage for mass and ^{19}F NMR spectral data.

(η^2-Olefin)tetracarbonylruthenium Complexes: Photochemical Syntheses from Dodecacarbonyltriruthenium and Quantum Yield Determinations

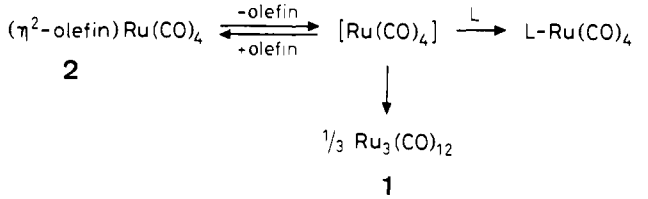
Friedrich-Wilhelm Grevels,*[1] Johannes G. A. Reuvers,*[1] and Josef Takats*[1]

Contribution from the Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany. *Received August 27, 1980*

Abstract: Photolysis of dodecacarbonyltriruthenium in the presence of excess olefin (methyl acrylate, dimethyl fumarate, dimethyl maleate, allyl acrylate, methyl vinyl ketone, and acrylonitrile) results in quantitative formation of (η^2-olefin)tetracarbonylruthenium complexes, some of which are isolated as white crystalline solids. Disappearance quantum yields, $\phi_{-Ru_3(CO)_{12}}$, are in the range of 0.003–0.12, depending on the olefin (methyl acrylate to dimethyl fumarate), its concentration, and the incident wavelength (λ = 313 and 395 nm). Mechanistic aspects are discussed. The infrared and NMR spectroscopic data of the (η^2-olefin)$Ru(CO)_4$ complexes indicate that the metal → π^*(olefin) interaction is strengthened in comparison with the analogous iron compounds, while the metal → π^*(CO) back-donation is decreased. Due to its moderate stability, (η^2-methyl acrylate)$Ru(CO)_4$ may be used as a source of $Ru(CO)_4$ thus providing another route to L–$Ru(CO)_4$ complexes.

In contrast to the various synthetic routes known for the complexes (η^2-olefin)$Fe(CO)_4$[2] no general high-yield synthesis of the analogous ruthenium compounds has been reported. (Ethylene)$Ru(CO)_4$[3] and (1-pentene)$Ru(CO)_4$[4] were generated by photolysis of $Ru_3(CO)_{12}$ in the presence of excess olefin and identified in situ by their infrared spectra. Recently, the quantum yield of such reactions was mentioned to be $\phi \approx 10^{-2}$, but no account was given of the actual isolation and characterization of these compounds.[4,5] (η^2-Olefin)$Ru(CO)_4$ complexes of ethyl acrylate and diethyl fumarate were prepared analogously and characterized by infrared and variable-temperature ^{13}C NMR spectroscopy and mass spectrometry;[6] however, it proved to be difficult to obtain analytically pure materials.

Scheme I



In this contribution we describe a convenient procedure for the photochemical preparation of (η^2-olefin)$Ru(CO)_4$ complexes from $Ru_3(CO)_{12}$. Quantum yields have been determined under various

(1) Address correspondence to any of the authors.
(2) King, R. B. In "The Organic Chemistry of Iron"; Koerner von Gustorf, E. A., Grevels, F.-W., Fischler, I., Eds.; Academic Press: New York, 1978; Vol. I, p 397.
(3) Johnson, B. F. G.; Lewis, J.; Twigg, M. V. *J. Organomet. Chem.* **1974**, *67*, C75.
(4) Austin, R. G.; Paonessa, R. S.; Giordano, P. J.; Wrighton, M. S. *Adv. Chem. Ser.* **1978**, *No. 168*, 189.
(5) Graff, J. L.; Sanner, R. D.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 273.
(6) Kruczynski, L.; Martin, J. L.; Takats, J. *J. Organomet. Chem.* **1974**, *80*, C9.

0002-7863/81/1503-4069$01.25/0 © 1981 American Chemical Society