chloride at 70–80°. Hydrogen chloride was added periodically to maintain saturation. After standing overnight, the mixture was filtered and mixed with water (3000 ml) containing $NaHCO_3$ and extracted with four 100-ml portions of ether. The ether solution was separated, dried ($MgSO_4$), and distilled. After removal of ether and a low-boiling (54–103°) fraction, the pentafluoropentane was collected at 103–105° to yield 6.3 g (19%). The infrared spectrum showed the CH stretch at 2960 cm^{-1} and C–F at 1265 and 1170 cm^{-1}. Unsaturation was absent. The proton nmr spectrum showed the $-CH_2-$ groups as a complex multiplet centered at τ 5.4, relative area = 4; –CHF– as two quintets (J = 6.0 cps) separated by 50 cps, relative area = 1; and $-CH_2F$ at τ 4.5 as two triplets (J = 5.8 cps) separated by 48 cps, relative area = 2.

Anal. Calcd for $C_5F_5H_7$: C, 37.1; F, 58.6; H, 4.3. Found: C, 37.3; F, 58.6; H, 4.4.

Photolysis Procedure.—Photolysis cells of approximately 1.8-ml capacity (1.5 cm long) were filled with a 0.2 M solution of the ketone in heptane (spectroquality), immersed in a quartz circulating water bath at 35 ± 0.5° and exposed to either a low-pressure mercury lamp (>90% uv output at 2537 Å) or a medium-pressure mercury lamp (25% uv output at 3100–3300 Å, 75% at 3300–3700 Å). Degassing (freeze–thaw technique) had no effect on quantum yields. Distilled quencher was added directly from a microliter syringe. Samples of 1 or 2 μl were taken every 20–60 min, depending on the lamp employed, over a period of several hours and analyzed by gas chromatography on a Carbowax 1500 column operated at 140° with a helium flow of 50 cc/min. Runs were carried to approximately 5–25% completion in the case of the quenching experiments utilizing the medium-pressure lamp and up to 75% completion when the 2537-Å lamp was used.

Four photolysis products were detected at retention times of 1.0, 2.2, 3.0, and 15.5 min. The first of these products was gaseous and was collected from the chromatograph in an evacuated infrared gas cell. The infrared spectrum bore a strong resemblance to that of 2,3,5,7,7,7-hexafluoro-1-heptene[10] exhibiting a =CF absorption at 1690 cm^{-1} and a CF_3 absorption at 1280 cm^{-1}. Insufficient material was obtained for further examination. The second eluted product had a retention time and ir spectrum identical with those of1,1,1,3,5-pentafluoropentane obtained by reduction of the corresponding iodide (see above). The product eluted at 3.0 min proved to be 1-fluoro-2-butanone by comparison with the sample prepared as described above. These materials agreed in retention times as well as infrared and nmr spectra (H^1 and F^{19}). The last eluted product was obtained in only trace amounts and highly contaminated with the starting ketone. However, the presence of a hydroxyl group was apparent in the infrared spectrum at 3200 cm^{-1}.

Registry No.—4,6,8,8,8 - Pentafluoro - 3 - octanone, 16408-87-0; 4,6,8,8,8-pentafluoro-3-octanone 2,4-dinitrophenylhydrazone, 16408-88-1; 1-fluoro-2-butanone, 453-10-1; 1-fluoro-2-butanone 2,4-dinitrophenylhydrazone, 580-05-2; 1,1,1,3,5-pentafluoropentane, 16408-89-2; fluorine, 7782-41-4.

Acknowledgment.—The author wishes to express his thanks to Mr. K. R. Weishaupt for performing many of the experiments in this work.

The Oxidation of Aldehydes in Alcoholic Media with the Caro Acid

A. NISHIHARA AND I. KUBOTA

Research Laboratory, Asahi Glass Company, Ltd.,
Hazawa-cho, Kanagawa-ku, Yokohama, Japan

Received December 14, 1967

The Caro acid (peroxymonosulfuric acid) has often been used as a characteristic oxidizing agent in the field of organic synthesis. It was early observed that the Baeyer–Villiger reaction occurred in the oxidation of carbonyl compounds with this oxidant as follows.[1]

$$R{-}CO{-}R' + H_2SO_5 \longrightarrow R{-}O{-}CO{-}R' + H_2O + H_2SO_4$$

Oxidation of acrolein in alcoholic media with hydrogen peroxide in the presence of selenium dioxide as catalyst was reported to give acrylates in 15–40% yield.[2] This method was investigated further in oxidation of other aldehydes in methanol or ethanol.[3] Methyl methacrylate was obtained also by the oxidation of methacrolein in methanol with t-butyl hydroperoxide in the presence of metal salt catalysts, such as $FeCl_2$ and $FeCl_3$.[4]

We wish to report that when aldehydes were oxidized with the Caro acid in the presence of alcohols the esters of corresponding acids could be obtained in high yield according to the equation

$$R{-}CHO + H_2SO_5 \xrightarrow{R''OH} RCOOR'' + H_2O + H_2SO_4$$

The results of these oxidations are summarized in Table I.

TABLE I

OXIDATION OF ALDEHYDES IN ALCOHOLS WITH THE CARO ACID

Aldehyde	Alcohol	Product	Conversion, %[a]	Selectivity, %[b]
Methacrolein	Methanol	Methyl methacrylate	94	91[c]
Methacrolein	Methanol	Methyl methacrylate	90	97[d]
Methacrolein	[e]	Methacrylic acid	65	29[d]
Methacrolein	Ethanol	Ethyl methacrylate	100	88[d]
Methacrolein	Isopropyl alcohol	Isopropyl methacrylate	83	55[d]
Acrolein	Methanol	Methyl acrylate	100	85[d]
Crotonaldehyde	Methanol	Methyl crotonate	100	63[d]
Propionaldehyde	Methanol	Methyl propionate	90	97[d]
Benzaldehyde	Methanol	Methyl benzoate	100	100[d]

[a] Conversion (%) = 100 (moles of aldehyde reacted/moles of aldehyde charged). [b] Selectivity (%) = 100 (moles of product/moles of aldehyde reacted). [c] The Caro acid was prepared from $(NH_4)_2S_2O_8$. [d] The Caro acid was prepared from H_2O_2 and H_2SO_4. [e] Ethyl ether was used instead of alcohol.

Mechanistically, it seems plausible that the Baeyer–Villiger reaction occurs first and esterification follows. Thus, the aldehyde is oxidized with the Caro acid to the corresponding carboxylic acid, which is esterified immediately with alcohol. However, when methacrolein was oxidized in ethyl ether instead of in methanol, the conversion of methacrolein and the selectivity of the main oxidation product (methacrylic acid) decreased remarkably. On the other hand, the rate of esterification of methacrylic acid with methanol in the presence of H_2SO_4 is much slower than that of oxidation of methacrolein in methanol with the Caro acid under the same condition of reaction (Figure 1). From these results, the above-mentioned mechanism involving intermediate formation of methacrylic acid followed by esterification could be excluded.

The direct formation of esters by the oxidation of primary alcohols with chromic acid was reported to occur by the reaction sequence, alcohol → aldehyde ⇌ hemiacetal → ester, rather than by the commonly ac-

---

(1) C. H. Hassall, *Org. Reactions*, **9**, 73 (1959).

(2) C. W. Smith and R. T. Holm, *J. Org. Chem.*, **22**, 746 (1957).

(3) M. Kitahara, T. Mitsui, and T. Hirayama, *Rika Gaku Kenkyusho Hokoku*, **38**, 81 (1962); *Chem. Abstr.*, **58**, 13788*a* (1963).

(4) Halcon International, Inc., Netherlands Patent Application, 6,412,904 (1965); *Chem. Abstr.*, **63**, 13085*e* (1965).

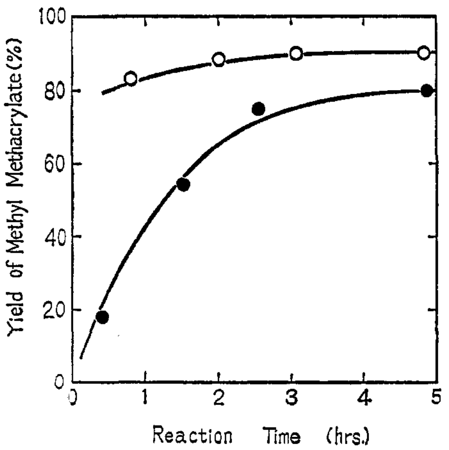
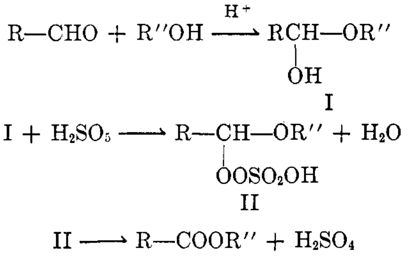


Figure 1.—Variation of yield of methyl methacrylate with reaction time in oxidation of methacrolein with the Caro acid in methanol (○) and in esterification of methacrylic acid with methanol in the presence of sulfuric acid (●); yield (%) = 100(moles of product/moles of aldehyde charged).

cepted path, alcohol → aldehyde → acid → ester.[5] It is most probable that this oxidation of aldehyde in alcoholic medium proceeds also through a hemiacetal peroxymonosulfate as Heywood, *et al.*, suggested in the oxidation of acetals with peracetic acid (Scheme I).[6]

Scheme I



$$\text{R—CHO} + \text{R}''\text{OH} \xrightarrow{\text{H}^+} \underset{\underset{\text{I}}{\text{OH}}}{\text{RCH—OR}''}$$

$$\text{I} + \text{H}_2\text{SO}_5 \longrightarrow \underset{\underset{\text{II}}{\text{OOSO}_2\text{OH}}}{\text{R—CH—OR}''} + \text{H}_2\text{O}$$

$$\text{II} \longrightarrow \text{R—COOR}'' + \text{H}_2\text{SO}_4$$

Experimental Section

Materials.—Methacrolein was prepared from propionaldehyde and paraformaldehyde in the manner described by Mitsui, *et al.*,[7] and purified by distillation (bp 66–68°). Propionaldehyde, acrolein, crotonaldehyde, and benzaldehyde were obtained commercially and used after distillation [bp 48–49, 52–53, 104–105, 74–76° (20 mm), respectively]. Methacrolein, crotonaldehyde, and acrolein were kept under refrigeration after the addition of 0.5 wt % hydroquinone. Other reagents were commercial materials used without further purification.

Preparation of the Caro Acid. A.—Ammonium persulfate (23.0 g) was added in small portions to 29.0 g of 85% H_2SO_4 maintained below 15° with stirring.

B.—H_2O_2 (3.9 g, 90%) was added dropwise to 25.0 g of concentrated H_2SO_4 maintained below 15° with stirring. The mixture was kept at room temperature for 2 hr.

Oxidation of Methacrolein in Methanol. A.—To a well-stirred mixture of 0.76 g of methacrolein and 12.9 g of methanol cooled to 10°, 5.6 g of the Caro acid prepared according to procedure A was added dropwise over a period of 2 min. During this addition, the internal temperature was kept below 10°. After stirring for 4 hr at 15°, the reaction mixture was diluted with water and extracted with ether. Methacrolein and methyl methacrylate in the combined ether extracts were analyzed quantitatively by gas chromatography. Benzene was used as the internal standard. The analysis was performed on a Yanagimoto GCG-220 at 80° with a helium flow rate of 50 ml/min and a 2.5-m column packed with 30% dioctyl phthalate on Celite 545. The conversion of methacrolein was 94% and the selectivity of methyl methacrylate was 91%. The gas chromatographic retention time of the methyl methacrylate agreed with that of an authentic sample.

B.—To a stirred mixture of 3.04 g of methacrolein and 79.5 g of methanol cooled to 15°, 12.2 g (equimolar to methacrolein) of the Caro acid prepared according to procedure B was added over a period of 10 min. During this addition, the internal temperature was kept below 15°. Stirring was continued at 15° and a 15-ml portion of the solution was sampled out at intervals. The aliquot parts were treated as described above and analyzed quantitatively by gas chromatography. The conversion of methacrolein after 3 hr was 90% and the selectivity of methyl methacrylate was 97%. The results obtained are shown in Figure 1 together with the results in the esterification reaction of methacrylic acid described below.

Methyl methacrylate isolated by gas chromatography with a Varian Aerograph 1525-B was identified by comparison of its infrared spectrum with that of an authentic sample, $n^{20}\text{D}$ 1.414.

Anal. Calcd for $C_5H_8O_2$: C, 59.98; H, 8.05. Found: C, 59.70; H, 8.02.

The other oxidations were carried out virtually as described above.

Esterification of Methacrylic Acid with Methanol.—To a stirred solution of 3.74 g of methacrylic acid and 79.5 g of methanol cooled to 15°, 10.6 g of concentrated H_2SO_4 was added over a period of 10 min. During the addition, the internal temperature was kept below 15°. Stirring was continued at 15° and a 15-ml portion of the solution was sampled out at intervals. The aliquot parts were treated as in the preceding experiment and yield of methyl methacrylate were determined by gas chromatographic analysis.

Oxidation of Methacrolein in Ethyl Ether.—A stirred mixture of 0.78 g of methacrolein and 21.6 g of ethyl ether was treated at 15° with 3.10 g of the Caro acid (prepared from H_2O_2 and H_2SO_4) over 3 hr. The solution was subjected to ether extraction and methacrylic acid in the ether extract was gas chromatographed at 135° on a 3-m column packed with 10% dioctyl sebacate on Diasolid S. Cyclohexanol was used as the internal standard. The conversion of methacrolein was 65% and the selectivity of methacrylic acid was 29%. Other products were not identified.

Oxidation of Benzaldehyde in Methanol.—To a stirred mixture of 10.6 g of benzaldehyde and 155 g of methanol cooled to 15°, 28.1 g of the Caro acid (equimolar to aldehyde) prepared according to procedure B was added dropwise over a period of 10 min. During the addition, the internal temperature was kept below 15°. After stirring for 3 hr at 15°, the mixture was treated as usual. The ethereal solution was analyzed by gas chromatography at 150° on a 3-m column packed with 10% dioctyl sebacate on Diasolid S. Cyclohexanol was used as the internal standard. The yield of methyl benzoate was quantitative. Methyl benzoate collected by gas chromatography was identified by comparison of its infrared spectrum with that of an authentic sample.

Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.78; H, 5.98.

Registry No.—Peroxymonosulfuric acid, 7722-86-3; methacrolein, 78-85-3; acrolein, 107-02-8; crotonaldehyde, 123-73-9; propionaldehyde, 123-38-6; benzaldehyde, 100-52-7.

---

[5] J. Cymerman Craig and E. C. Horning, *J. Org. Chem.*, **25**, 2098 (1960).

[6] D. L. Heywood and B. Phillips, *ibid.*, **25**, 1699 (1960).

[7] T. Mitsui, M. Kitahara, and Y. Miyatake, *Rika Gaku Kenkyusho Hokoku*, **38**, 205 (1962); *Chem. Abstr.*, **59**, 3762*d* (1963).

Reduction of Some Sulfonium Salts with Lithium Aluminum Hydride

S. Ašperger, D. Stefanovi´, D. Hegedić,
D. Pavlović, and L. Klasinc

Institute "Rudjer Bošković," Zagreb,
and Faculty of Pharmacy and Biochemistry,
University of Zagreb, Zagreb, Yugoslavia

Received December 13, 1967

Since Schmid and Karrer[1] performed the first reduction of some cyclic ammonium salts with lithium

---

[1] H. Schmid and P. Karrer, *Helv. Chim. Acta*, **32**, 960 (1949).