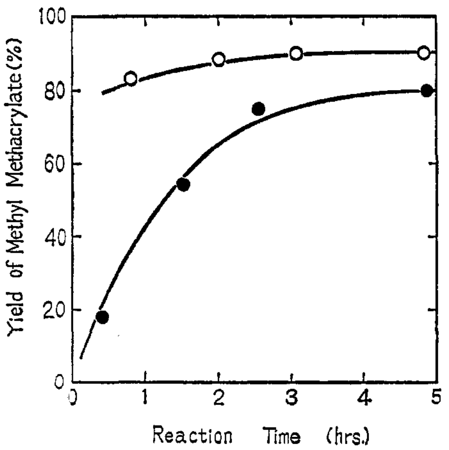
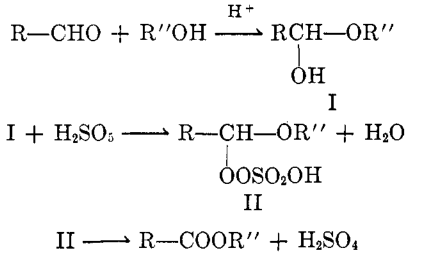


Figure 1.—Variation of yield of methyl methacrylate with reaction time in oxidation of methacrolein with the Caro acid in methanol (○) and in esterification of methacrylic acid with methanol in the presence of sulfuric acid (●); yield (%) = 100(moles of product/moles of aldehyde charged).

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



$$\mathrm{R{-}CHO + R''OH \xrightarrow{H^+} R\underset{\underset{\displaystyle OH}{|}}{C}H{-}OR''} \quad \mathrm{I}$$

$$\mathrm{I + H_2SO_5 \longrightarrow R{-}\underset{\underset{\displaystyle OOSO_2OH}{|}}{C}H{-}OR'' + H_2O} \quad \mathrm{II}$$

$$\mathrm{II \longrightarrow R{-}COOR'' + H_2SO_4}$$

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, $n^{20}\mathrm{D}$ 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.

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Reduction of Some Sulfonium Salts with Lithium Aluminum Hydride

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

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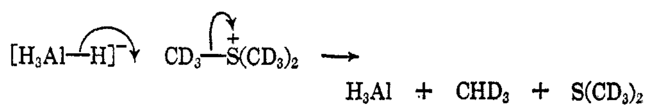
[1] H. Schmid and P. Karrer, *Helv. Chim. Acta*, **32**, 960 (1949).

aluminum hydride, the reductions of phosphonium,[2] aliphatic ammonium,[3] and stibonium salts[4] have also been reported. Surprisingly enough, sulfonium salts have not been investigated. We previously observed[5] that a liquid reduction product mixture obtained by the reduction of 2-phenylethyldimethylsulfonium bromide with lithium aluminum hydride contained mainly methyl-2-phenylethyl sulfide.

A more thorough investigation of lithium aluminum hydride reductions of some sulfonium salts is now reported.

Reduction of Trimethylsulfonium Bromide.—The sulfonium salt suspended in diethylene glycol diethyl ether was reduced with lithium aluminum hydride at 45° for 2.5 hr, and at 60° for 4.5 hr, respectively. The analysis of the gaseous products by gas chromatography and the analysis of the reaction solution showed methane and dimethyl sulfide to be the only reduction products.

The deuterated sulfonium salt was also reduced with $LiAlH_4$. From the gaseous products, methane was isolated and analyzed by mass spectrometry. The mass spectrum contained an intensive mass of 19 mass units corresponding to CHD_3. The undeuterated sulfonium salt was also reduced with $LiAlD_4$. The methane had the main mass of 17 mass units, corresponding to CH_3D. No methane of the formula CH_2D_2 with mass 18 could be detected. This suggests that a simple displacement takes place, *e.g.*, in case of the deuterated salt



$$[H_3Al-H]^- \quad CD_3-\overset{+}{S}(CD_3)_2 \longrightarrow H_3Al + CHD_3 + S(CD_3)_2$$

(in the equation H_3Al is written only formally)

It is known[6] that sulfonium salts exchange hydrogens very rapidly, while ammonium salts exchange hydrogens extremely slowly, which has been explained in terms of d-orbital resonance occurring at the sulfonium salts. Since sulfonium salts are more easily reduced with lithium aluminum hydride than are ammonium salts, one could assume that the reduction occurs at the intermediate zwitterion in which a partial neutralization of charge by electron drift from the carbon atom into the d-orbital of the sulfur atom takes place, giving the carbon–sulfur bond considerable double-bond character. If it were so, the reduction of deuterated trimethylsulfonium salt would most probably yield methane of the formula CH_2D_2 with simultaneous evolution of an equivalent quantity of hydrogen (HD). This is not the case.

Reduction of 2-Phenylethyldimethylsulfonium Bromide.—The reductions were carried out in diethyl ether at 35° for 2.5 hr and overnight at room temperature, and also in tetrahydrofuran at 65° for 2.5 hr. The salt was again in suspension. The main reduction products were methyl-2-phenylethyl sulfide and methane. Small quantities of ethylbenzene and dimethyl sulfide (less than 5%) were also detected by gas chromatography and by mass spectrometry. The products are most probably formed by analogous hydride ion attack as suggested above.

In solvents dried with no special precautions, containing the usual amount of moisture of about 0.05%, the base-catalyzed elimination occurred during reduction, which yielded up to 40% of styrene. When the solvent was very carefully dried by several distillations over sodium and subsequently dried over Molecular Sieves 4A, no styrene could be detected in the reduction products.

In order to check the drying procedure, water containing tritium was added to the dry solvent and the drying procedure repeated. The specific activity of the solvent indicated that it contained about 0.0001% of water.

Cram found[7] that the reduction of *p*-toluenesulfonate of 3-phenyl-2-butanol with lithium aluminum hydride in diethyl ether yielded 2-phenylbutane, but elimination also occurred giving 2-phenyl-2-butene. We have carried out the same reaction applying the drying procedure of the solvent mentioned above (which practically excludes the base catalysis) and have found that the elimination still takes place. Gas chromatography shows that the ratio of 2-phenylbutane to 2-phenyl-2-butene is 3:1.

On the other hand, in the reduction of 2-phenylethyl *p*-toluenesulfonate (primary α carbon) with lithium aluminum hydride in dry diethyl ether, we could not find any elimination products.

It was interesting to see whether sulfonium salts of a similar type, having sulfur bonded to the secondary α-carbon atom, would also undergo elimination during the reduction with lithium aluminum hydride. It was found that the only products of the reduction of 3-phenyl-2-butyldimethylsulfonium bromide were methane and the corresponding sulfide. 2-Phenyl-2-butene was not detected.[8]

Cram suggested[7] that, in the reaction of 3-phenyl-2-butyl *p*-toluenesulfonate with lithium aluminum hydride, olefin is formed by a bimolecular mechanism. However, the fact that the mentioned tosylate yields olefin with lithium aluminum hydride and the corresponding sulfonium salt does not could be better explained by assuming that *p*-toluenesulfonate reacts *via* a salt-promoted ionization[9] and olefin is formed *via* a carbonium ion process, while sulfonium salt reacts by a displacement process.

2-Phenylethyltrimethylammonium iodide was also reduced with lithium aluminum hydride in tetrahydrofuran at 65° for 60 hr. Dimethyl-2-phenylethylamine and methane were the main products (about 95%). Ethylbenzene and trimethylamine were also detected (about 5%). Again, in very dry tetrahydrofuran, no elimination could be observed, but, in tetrahydrofuran containing about 0.05% of water, 23% of styrene was found.

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Experimental Section

A Nier-type mass spectrometer with a resolution of 1:300, produced at the Institute "Jožef Stefan," Ljubljana, Yugoslavia, was used. Gas–liquid partition chromatographic analyses were performed using a Perkin-Elmer 154D instrument, and a Wilkens Instrument and Research A-90-C machine, respectively.

Materials.—Trimethylsulfonium bromide was prepared as described by Cooper, Hughes, Ingold, and Mac Nulty,[10] 2-phenylethyldimethylsulfonium bromide by the procedure of Saunders and Ašperger,[11] 2-phenylethyltrimethylammonium iodide by the procedure of von Braun and Neumann,[12] 2-phenylethyl-*p*-toluenesulfonate as described by Klamann,[13] and 2-phenyl-3-butyl-*p*-toluenesulfonate and 2-phenyl-2-butene by the procedures of Cram.[7,14] 2-Phenylbutane was prepared from 2-phenyl-2-butene by catalytic hydrogenation using palladium on activated charcoal (10%) as catalyst.

Deuterated Materials.—Deuterated trimethylsulfonium bromide was prepared by direct hydrogen exchange in 7.5 M sodium deuteroxide solution, following the procedure of Doering and Hoffmann.[6] The exchange is practically complete.

Drying of the Solvent.—Diethyl ether and tetrahydrofuran were dried over sodium, distilled, dried over Molecular Sieves 4A (activated during 8 hr at 300° and 1-torr pressure), and distilled. Drying over molecular sieves was repeated several times. This drying procedure was tested by the addition of known amount of water containing tritium (200 mCi/ml) to the dry solvent. After the drying procedure was repeated, the specific activity of the solvent showed that there was only about 0.0001% of water in the solvent.

Reduction with Lithium Aluminum Hydride.—The solution of lithium aluminum hydride was prepared by shaking of 6.0 g of $LiAlH_4$ with 50 ml of dry solvent for 4 hr. The solid was allowed to settle and the liquid was decanted. The concentration of lithium aluminum hydride in ethereal solution was estimated by the method of Felkin.[15]

A mixture consisting of lithium aluminum hydride in large excess to the substance was stirred in dry solvent at the appropriate temperature. Aqueous sodium hydroxide solution (10%) was then added. The products of the reduction were isolated by extraction with pentane and the organic layer was washed, dried, and concentrated.

Analysis of Products.—The gaseous products of the reduction were collected in a liquid air trap, purified on a vacuum line, and analyzed by mass spectrometry. By this method the following reaction products were estimated: methane, deuterated methane (CH_3D), dimethyl sulfide, and trimethylamine.

Gas–liquid partition chromatography was used for the analysis of concentrated pentane extract. The following reaction products were estimated (by comparison with the pure substances): methane (on 0.25 in. × 2 m stainless steel column packed with silica gel + 2% di-2-ethylhexyl sebacate using flame ionization detector), dimethyl sulfide, ethylbenzene, styrene, methyl-2-phenylethyl sulfide, 2-phenylbutane, and 2-phenyl-2-butene (on 0.25 in. × 1.5 m stainless steel column packed with 15% silicone GE SF-96 on 60–80 mesh firebrick using thermal conductivity detector), trimethylamine, and dimethyl-2-phenylethylamine (on 0.25 in. × 2 m stainless steel column packed with 10% silicone oil DC-200 on 60–80 mesh Chromosorb W using thermal conductivity detector).

Registry No.—Lithium aluminum hydride, 1302-30-3; trimethylsulfonium bromide, 676-84-6; 2-phenylethyldimethylsulfonium bromide, 16315-48-3.

Acknowledgment.—The authors thank Professor W. H. Saunders and Professor S. Borčič for helpful discussion.

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Heterogeneous Photosensitization

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Recently Leermakers and James[1] described the use of a solid, polyvinylphenyl ketone, to photosensitize piperylene, norbornadiene, and myrcene in the liquid phase. As pointed out by these authors, liquid–solid or gas–solid cross phase photosensitization has the particular advantage that there are no problems of separation of the sensitizer from the products or reactants.

We have been investigating the cross phase photosensitization of the piperylenes and 1,3-cyclohexadiene in the vapor phase by thin polymeric films deposited on the walls of quartz or Pyrex photolysis reactors.

The photosensitizer films are produced by the *in situ* photolysis of suitable monomers in the gas or vapor phase. For example, the photolysis of 5 torr of benzaldehyde in a Pyrex reactor with the filtered light (0.5 cm of 1 M $CuSO_4$) of a Philips HP 125 medium-pressure Hg lamp for 30 min produces a polymeric film which was still active as a photosensitizer after more than 50 hr of service. This film does not have the same photochemical properties as benzaldehyde (*vide infra*) in sharp contrast to the polyvinylphenyl ketone sensitizer described by Leermakers and James[1] which seems to have approximately the same photochemical properties as the parent phenylvinyl ketone.

Control experiments performed before deposition of the polymeric film in the reactor showed that the dienes were totally unaffected by the light entering the cell; further blank experiments at 50° in the presence of the film for 24 hr indicated the total absence of dark reactions. Photodimerization of 1,3-cyclohexadiene, slower photodimerization of piperylene, and rapid *cis–trans* isomerization of the piperylenes were observed in the presence of the polymeric film. With either *cis-* or *trans*-1,3-pentadiene as starting material a photostationary *trans/cis* ratio of 4:1 was obtained after several hours irradiation. This ratio, much larger than that obtained in the liquid phase photosensitization of piperylene by benzaldehyde (triplet energy = 72 kcal/mol, ratio = 1.23),[2] suggests from the correlation of Hammond, Turro, and Leermakers[2] that the triplet energy of the polymeric films is 55 ± 5 kcal/mol. This latter result is substantiated by the fact that the polymeric film does not sensitize dimerization of *cis–trans* isomerization of 1,2-dichloroethylene[3] where the triplet energy is ~70 kcal/mol.[4]

The present results clearly indicate the practicability of photosensitization of molecules in the vapor phase

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[3] Two sets of experiments were carried out with initial *cis/trans* ratios of 2.5:1 and 7:1, respectively. These starting ratios are similar to the photostationary states found by Hammond, *et al.*,[2] for acetophenone (E triplet = 74 kcal/mol, *cis/trans* ratio = 3.1:1) and for benzophenone (E triplet = 70 kcal/mol, *cis/trans* ratio = 4.5:1) photosensitizations of the dichloroethylenes in the liquid phase. The use of two different *cis/trans* ratios eliminates the possibility that one may be the photostationary state.

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