in ice and the precipitated 3-monoketal VI (5.28 g. with m.p. 227–230°) was collected. The filtrate was diluted with benzene and was then washed with sodium bicarbonate solution and water, dried and evaporated. Crystallization of the residue from acetone furnished another 1.81 g. of the monoketal VI with m.p. 230–233° (total yield 7.09 g., 62%). Further crystallization from acetone led to the analytical specimen with m.p. 234–236°, $[\alpha]^{20}\text{D}$ +8° (pyridine), $\lambda_{\text{max.}}$ 238 mμ (log ε 4.03), $\nu_{\text{max.}}$ 1656 cm.$^{-1}$.

Anal. Calcd. for $C_{23}H_{32}O_3$: C, 77.49; H, 9.05. Found: C, 77.31; H, 8.69.

3-Ethylenedioxy-Δ^5-pregnen-20-one (Progesterone 3-Cycloethylene Ketal) (I). (a) From Progesterone (II).—A mixture of 5 g. of progesterone and 0.2 g. of *p*-toluenesulfonic acid dihydrate in 80 cc. of methylethyldioxolane (freshly distilled over lithium aluminum hydride) was heated to boiling (580 mm.) and then distilled for 10 minutes (25 cc. of distillate collected). The solution was diluted with benzene and was then washed with sodium bicarbonate solution and water, dried and evaporated. The oily residue ($\lambda_{\text{max.}}$ 240 mμ, log ε 3.96) was chromatographed on 250 g. of neutral alumina. The fractions eluted with hexane and hexane–benzene (9:1) yielded a small amount (*ca.* 50 mg.) of progesterone bis-cycloethyleneketal with m.p. 179–180°, $[\alpha]^{20}\text{D}$ −29° (chloroform) [reported[5] m.p. 180–181°, $[\alpha]^{24}\text{D}$ −27° (chloroform)]. The fractions eluted with hexane–benzene (6:4 to 4:6) on crystallization from acetone–hexane produced 1.41 g. (25%) of the 3-monoketal I with m.p. 180–181°, $[\alpha]^{20}\text{D}$ +28° (chloroform), +53° (pyridine), no high-intensity absorption in the ultraviolet, $\nu_{\text{max.}}^{\text{mull}}$ 1700 cm.$^{-1}$ A m.p. depression of *ca.* 20° was observed on admixture with the diketal.

Anal. Calcd. for $C_{23}H_{34}O_3$: C, 77.05; H, 9.56. Found: C, 77.32; H, 9.78.

When the distillation time was increased to 30 minutes, the yield of the monoketal I was decreased to 22% and that of the diketal increased to 8%.

(b) **From 3-Ethylenedioxy-Δ^5-pregnen-20β-ol (IV).**—Chromium trioxide (0.3 g.) was added slowly with stirring and cooling to 6 cc. of dry pyridine (temperature kept below 30°). A solution of 0.3 g. of 3-ethylenedioxy-Δ^5-pregnen-20β-ol (IV) in 6 cc. of pyridine was then added dropwise with continued cooling and the mixture was allowed to stand at room temperature overnight. Water and then equal parts of benzene and ether were added, the mixture was filtered through celite and the organic layer was well washed with water, dried and evaporated. Crystallization from acetone–hexane furnished 0.18 g. of the ketal I with m.p. 173–175°, $[\alpha]^{20}\text{D}$ +50° (pyridine). Identity with that prepared by method a was established by mixture m.p. determination and infrared comparison.

(c) **From 3-Ethylenedioxy-Δ^{5,16}-pregnadien-20-one (VI).**—A solution of 3 g. of 3-ethylenedioxy-Δ^{5,16}-pregnadien-20-one (VI) in 250 cc. of ethyl acetate was shaken in hydrogen with 0.3 g. of a 10% palladium–calcium carbonate catalyst at 21° and 585 mm. In 5 hours 1.02 moles of gas had been absorbed and uptake had stopped. Removal of catalyst and solvent followed by crystallization of the residue from acetone–hexane produced 2.74 g. (91%) of the ketal I with m.p. 178–180°, $[\alpha]^{20}\text{D}$ +52° (pyridine), no high-intensity absorption in the ultraviolet. Identity with samples prepared by methods a and b was confirmed by mixture m.p. and infrared comparison.

KILOMETRO 13½ DE LA CARRETERA A TOLUCA
APARTADO POSTAL 2679
MEXICO, D. F.

Preparation of Tetraethylene Glycol Dimethacrylate

BY JOHN V. SCHMITZ

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Various methods are available for the preparation of dimethacrylate esters of glycols.[1] These include reaction of the glycol with methacrylic acid, methacrylyl chloride or methacrylic anhydride or transesterification with methyl methacrylate. Of these, the last reaction is the most attractive from the standpoint of economics and convenience. However, in the preparation of tetraethylene glycol dimethacrylate (TEGMA), it was found that the usual procedures of transesterification were not satisfactory. Only moderate yields of TEGMA were obtained using hydroquinone or *o*-phenylenediamine as inhibitors under acidic or basic conditions, and the reactions were frequently accompanied by polymerization and gelation of the TEGMA.[2] In addition, it was difficult to remove those inhibitors, when they were used in high concentration, from TEGMA, which cannot be purified by distillation (b.p. > 160° at <1 mm.) or crystallization (forms a glass at −65°).

For these reasons, two new procedures were devised for the transesterification reaction. These methods involved the use of inhibitor–catalyst combinations of oxygen–sodium alcoholate or picric acid–sulfuric acid. The former is preferred since it gives somewhat faster rates of reaction and better yields. Both of the inhibitors prevented polymerization effectively and could be conveniently and completely removed to give good yields of satisfactory TEGMA.

Oxygen has been successfully used as an inhibitor of the polymerization of methyl methacrylate and several other monomers.[3] However, it has not been used widely as an inhibitor during the synthesis or chemical reactions of reactive vinyl monomers.[4] Contrariwise, in many such reactions oxygen is rigidly excluded. The present work indicates that the use of oxygen as a transient inhibitor can offer advantages.

The use of oxygen as an inhibitor leads to the formation of peroxidic oxidation products.[3] In our work, peroxides were substantially absent in the products formed under basic conditions. However, when sulfuric acid–air was used as the catalyst–inhibitor system, the TEGMA which was produced contained reactive peroxides (0.3% active oxygen as determined by the acetic acid–potassium iodide method[5]). These active peroxides were capable of inducing the polymerization of TEGMA in the absence of oxygen.

Base-catalyzed Transesterification Using Oxygen as Inhibitor.—Methyl methacrylate (100 g., 1.0 mole, coml.), tetraethylene glycol (59.5 g., 0.30 mole, redistilled), sodium hydride (1.3 g., 0.05 mole) and benzene (100 g., C.P.) were charged into a flask fitted with a fractionating column. Air (0.5 l./min.) was passed into the stirred reaction mixture which was immersed in a heated oil-bath (bath temperature, 95–100°; internal temperature, 81–82°). The take-off temperature of the benzene–methanol azeotrope was maintained at 54° for the first hour and below 70° for two additional hours, at the end of which nearly the theoretical amount of methanol had been collected. More benzene

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[1] R. S. Corley, "Esters of Methacrylic Acid Other than Methyl Methacrylate," in E. R. Blout and H. Mark, "Monomers," Interscience Publishers, Inc., New York, N. Y., 1951.

[2] Ethylene glycol dimethacrylate, the parent compound of this series gels at only 2.9% reaction. *Cf.* C. Walling, THIS JOURNAL, **67**, 441 (1945).

[3] F. A. Bovey and I. M. Kolthoff, *Chem. Revs.*, **42**, 502–505 (1948).

[4] There is a report in the patent literature of the use of oxygen as an inhibitor during the preparation of methacrylic acid or methyl methacrylate from acetone cyanhydrin; H. R. Dittmar, U. S. Patent 2,373,464 (1945).

[5] W. E. Cass, THIS JOURNAL, **68**, 1981 (1946).

(100 g.) was added during the reaction to replace that removed by distillation.

The reaction mixture was allowed to cool while it was being neutralized by carbon dioxide (vented into the air stream from 50–100 g. of Dry Ice maintained in a filter flask) diluted with air. The neutralization was completed within one hour as indicated by a neutral reaction to moist Alkacid test paper. Insoluble impurities were removed by centrifugation and soluble colored impurities were removed from the centrifugate by adsorption on a four-inch column of activated alumina previously moistened with benzene. Volatile solvents were removed at room temperature under reduced pressure. The yields, based on tetraethylene glycol, were 75–80% of nearly colorless TEGMA, n^{20}_{D} 1.4631, d^{20}_{20} 1.087.

Anal. Calcd. for $C_{16}H_{26}O_7$: C, 58.2; H, 7.9; sapon. equiv., 165; M_D 83.4. Found: C, 57.8; H, 8.2; sapon. equiv., 166, 169; M_D 83.4.

Conductivity measurements (1.14×10^{-8} mho-cm. at 1 Kc.) indicated that ions from the basic catalyst had been largely removed by the purification procedure.

Acid-catalyzed Transesterification Using Picric Acid as Inhibitor.—The same apparatus was used as in the base-catalyzed reaction. The charge consisted of methyl methacrylate (100 g., 1.0 mole, coml.), benzene (75 g., C.P.) and concd. sulfuric acid (10.0 g., 0.098 mole) and picric acid (0.10 g.). The mixture was distilled under hydrogen until no more water was evolved. Tetraethylene glycol (59.5 g., 0.30 mole, redistilled) was added and the reaction was carried out as above for 3.5 hours using hydrogen as an inert atmosphere. At the end of this period nearly the theoretical amount of methanol had been collected. An additional quantity of benzene (50 g.) was added during the reaction.

The reaction mixture was allowed to cool and sodium carbonate (24 g., 0.20 mole) and water (10 g.) were added with vigorous stirring. After 15 minutes there was a sudden color change to the bright yellow color of the picrate ion which indicated complete neutralization. The mixture was diluted with cyclohexane (150 ml.) and all of the insoluble impurities coagulated into a sticky mass leaving a clear supernatant liquid layer which was removed by decantation. Remaining colored impurities were removed from the solution by adsorption on a 4-inch column of activated alumina. Removal of volatile materials under reduced pressure gave a 65–70% yield of TEGMA, n^{20}_{D} 1.4620, sapon. equiv., 164–165.

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RESEARCH LABORATORY
GENERAL ELECTRIC COMPANY
SCHENECTADY, NEW YORK

Octane-1,1,1,8,8,8-d_6

BY ANDREW STREITWIESER, JR.

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An attractive approach to the assignment of the vibrations of normal aliphatic hydrocarbons into methyl and methylene motions is through the use of a hydrocarbon in which the terminal methyl groups have been replaced by methyl-d_3 groups. Octane-1,1,1,8,8,8-d_6 was thought to be a suitable choice for such a compound because of the length of its methylene chain and of its convenient physical properties.

Dimethyl suberate was reduced with lithium aluminum deuteride to 1,8-octanediol-1,1,8,8-d_4. The glycol was converted to the di-*p*-toluenesulfonate which was further reduced with lithium aluminum deuteride in boiling ether. This final reduction was, however, very sluggish and gave poor yields. More vigorous conditions were considered to be unsatisfactory because of the possible occurrence of undesirable side reactions.[1] The deuterogenolysis of the dihalide may well be a better route at this point.

The density of the product, d^{25}_{4} 0.7354, is close to that calculated for octane-d_6 assuming constancy of molecular volume, d^{25}_{4} 0.7351. Mass spectrographic analysis indicated 90.9% octane-d_6, 7.7% -d_5, 0.6% -d_4 and 0.47% -d_7.[2] The infrared spectrum and its detailed interpretation will be presented elsewhere.[3]

Experimental[4]

1,8-Octanediol-1,1,8,8-d_4.—To 2.0 g. of lithium aluminum deuteride[5] in dry ether was added with vigorous stirring 10.1 g. of dimethyl suberate[6] dissolved in dry ether. Dilute hydrochloric acid was added until the solid inorganic salts separated leaving a clear ether layer which was decanted. The salts were washed with ether and the combined ether layers were evaporated leaving 7.8 g. of crude glycol. Continuous ether extraction of a dilute acid solution of the inorganic salts gave a further 0.3 g. The combined crops were recrystallized from benzene–hexane giving 5.9 g. (79%) of small white crystals, m.p. 56.0–58.0°. A further recrystallization from benzene–hexane raised the m.p. to 58.0–58.5°.

1,8-Octanediol-1,1,8,8-d_4 Di-*p*-toluenesulfonate.—A solution of 9.73 g. of 1,8-octanediol-1,1,8,8-d_4 in 100 cc. of pyridine was cooled to −10° and 27.7 g. of *p*-toluenesulfonyl chloride was added. After standing in an ice–salt-bath for an hour with frequent swirling, 100 cc. of water was added in portions such that the temperature was kept below 10°. The white granular precipitate was filtered and washed with water. The filtrate contained 4 g. of the monotosylate as a heavy oil which, on further treatment with 5.5 g. of *p*-toluenesulfonyl chloride in the same way, gave an additional quantity of product. After drying, the combined yield of product, m.p. 68.0–70.8°, was 24.9 g. (84%).

Undeuterated material was prepared in the same way from diol prepared by the reduction of dimethyl suberate with lithium aluminum hydride. After one crystallization from benzene the m.p. was 72.8–73.3°.

Anal. Calcd. for $C_{22}H_{30}O_6S_2$: C, 58.1; H, 6.7; S, 14.1. Found: C, 57.9; H, 6.7; S, 14.0.

Octane-1,1,1,8,8,8-d_6.—The ditosylate (20.7 g.) was extracted in a Soxhlet apparatus by a dry ether solution of 1.0 g. of lithium aluminum deuteride. After two days of refluxing the deuteride apparently had reacted completely. Dilute hydrochloric acid was added and the ether layer was separated. Filtration of the aqueous phase gave 3.4 g. of unreacted ditosylate. The ether solution was washed with water and dried with potassium carbonate. The residue after distillation of the ether was mixed with 100 cc. of pure pentane. Filtration of this mixture gave an additional 2.7 g. of unreacted ditosylate. After removal of pentane from the filtrate the residue was distilled from a small flask yielding 0.6 cc. of a crude octane fraction, b.p. 115–124°. The considerable residue from this distillation was undoubtedly the unreacted *p*-toluenesulfonate of 1-octanol-1,1,8,8,8-d_5.

The octane fractions of several runs were combined and redistilled. The distillate was shaken with cold concentrated sulfuric acid,[7] then washed and dried. Distillation gave 1.1

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(1) D. S. Noyce, private communication.

(2) We are indebted to Dr. J. C. Guffy and his associates at the California Research Corp., Richmond, Calif., for the mass spectrum and its analysis.

(3) G. C. Pimentel and W. A. Klemperer, *J. Chem. Phys.*, in press.

(4) Melting points were taken in a Hershberg apparatus and are corrected. Analysis by the Microanalytical Laboratory of the University of California.

(5) Obtained from Metal Hydrides, Inc., Beverly, Mass., on allocation by the United States Atomic Energy Commission.

(6) A. I. Vogel, *J. Chem. Soc.*, 333 (1934).

(7) This treatment is not expected to cause exchange or isomerization of the octane; *cf.*, D. P. Stevenson, *et al.*, THIS JOURNAL, **74**, 3269 (1952).