

the extract was concentrated to yield 10 g more of organic material.

The other reactions catalyzed with HF were run in the same apparatus, with the olefin being added from a polyethylene dropping funnel instead of the gas inlet tube.

Acid-Catalyzed Reactions of *p*-Cymene with Diisobutylene.

Run 5a.—This run was like run 1b except that the olefin (56 g, 0.50 mol) was added from a pressure-equalizing funnel over a 1-hr period. The yield of products was 77.6 g. The above description, modified as given in Table I, is typical of all the reactions using di-, tri-, and tetraisobutylene.

Preparation of 1,3,3,6-Tetramethyl-1-neopentylindan (8) from *p*-Cymene and Diisobutylene. **Run 5c.**—In a 5-l. Morton flask equipped with a 2-l. dropping funnel and a thermocouple were placed 1100 g (8.2 mol) of *p*-cymene. This was cooled to 5° and sulfuric acid, 72 g, was introduced. Diisobutylene, 1480 g (13.2 mol), was added dropwise to the reaction mixture, which was stirred with a large Vibromixer. The temperature was kept below 10° throughout the 2.5 hr required to add the olefin and during the additional 3 hr the mixture was stirred. The mixture was worked up as in run 1b. Glc analysis showed a 43% yield of 8.

A distillation fraction [bp 82–88° (0.5 mm)] from run 5c in which 8 was concentrated was subjected to preparative glc at 150° using the apparatus previously described. The material collected was distilled and then passed through a column of silica gel and acidic and basic alumina to give 92 g of 8 (see Table II).

Registry No.—1, 99-87-6; 2, 81-03-8; 3, 29577-13-7; 4, 29641-87-0; 5, 4834-28-0; 7, 29577-15-9; 8, 29577-16-0; 9, 29577-17-1; 10, 1153-36-2; 12, 29577-19-3; 13, 29577-20-6; 14, 29577-21-7; 15, 29577-22-8; 16, 29641-88-1; 17, 29577-23-9; 19, 29577-24-0; 20, 29577-25-1; isobutylene, 115-11-7; *o*-cymene, 527-84-4; *m*-cymene, 535-77-3.

Acknowledgments.—We are grateful to the American Petroleum Institute for generous support of API Research Project 58A and to the Research Foundation, Oklahoma State University, for their assistance. We thank Dr. O. C. Dermer for having read the manuscript.

Acid-Catalyzed Reactions of Propioloophenone and 2-Ethynyl-2-phenyl-1,3-dioxolane with Ethylene Glycol¹

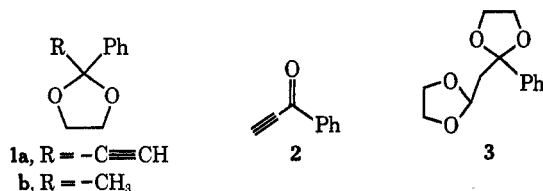
R. R. FRAME* AND W. FAULCONER

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73069

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An attempt to prepare 2-ethynyl-2-phenyl-1,3-dioxolane (1a) from propioloophenone (2), *p*-toluenesulfonic acid, and excess ethylene glycol resulted instead in the formation of 2-phenyl-2,2'-methylenebis-1,3-dioxolane (3) and/or 2-methyl-2-phenyl-1,3-dioxolane (1b). With a small amount of *p*-toluenesulfonic acid the former product predominated, but with equimolar propioloophenone and acid only the latter was formed. It was found that 3 could be converted to 1b with equimolar *p*-toluenesulfonic acid. A synthesis of 1a from 2-(1-bromoethyl)-2-phenyl-1,3-dioxolane (5) is described. Compound 1a was found to be stable to the conditions which converted 2 to 3. This observation and certain spectroscopic evidence indicate that 3 is formed from 2 *via* 1-oxo-1-phenyl-3-(1,3-dioxolane)propane (4).

An attempt to prepare 2-ethynyl-2-phenyl-1,3-dioxolane (1a) from propioloophenone (2), a small amount of anhydrous *p*-toluenesulfonic acid, and excess ethylene glycol in refluxing benzene with constant removal of benzene-water azeotrope yielded instead 2-phenyl-2,2'-methylenebis-1,3-dioxolane (3) (84%). The acetylenic proton of 1a was not observed in the nmr spectrum of the crude product from this reaction, but this spectrum did exhibit a singlet with a chemical shift identical with that of the methyl group of 2-methyl-2-phenyl-1,3-dioxolane (1b). Integration revealed that the 3:1b ratio was 13:1. When an equivalent



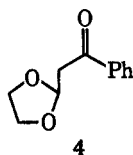
amount of 2 and anhydrous *p*-toluenesulfonic acid and excess ethylene glycol were similarly reacted, 1b was the only product that could be isolated (52%). The nmr spectrum of the crude product from this reaction revealed the absence of 1a and 3. Finally, when an equivalent amount of 3 and anhydrous *p*-toluenesulfonic acid and excess ethylene glycol were similarly re-

acted, 1b again was the only product that could be isolated (35%).

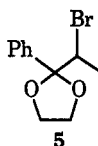
When equivalent amounts of 2 and ethylene glycol and a catalytic quantity of anhydrous *p*-toluenesulfonic acid were refluxed in benzene, the product was a multicomponent oil. Its nmr spectrum contained a large multiplet, the chemical shift of which was roughly the same as that previously found for the OCH₂CH₂O systems of 3 and 1b. This spectrum also contained the characteristic doublet (τ 7.79) and triplet (τ 5.18) of 3, a second doublet (τ 6.76) and triplet (τ 4.67), and a signal in the aromatic region. Two components, one an oil and the other a solid, resulted when this mixture was subjected to plc. Nmr analysis revealed the solid to be 2. It was not detected in the nmr of the original oil since its acetylenic proton falls in the same region as the dioxolane ring protons. The new oil exhibited a carbonyl absorption at 5.84 μ . Further attempts to separate it by plc resulted in small amounts of pure 3, but the carbonyl-containing substituent could not be isolated. The nmr of this oil again exhibited a pair of doublets and a pair of triplets, and aromatic plus dioxolane ring protons. The areas under the signals due to the aromatic and dioxolane ring protons were greater than would be predicted were they to have arisen from 3 alone, but what one would predict if the second component possessed one phenyl group and one dioxolane ring. We feel the spectroscopic evidence strongly implies that the third component was 1-oxo-1-phenyl-3-

(1) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971.

(1,3-dioxolane)propane (4). The three yields follow: 2 (30%), 3 (34%), and 4 (14%).



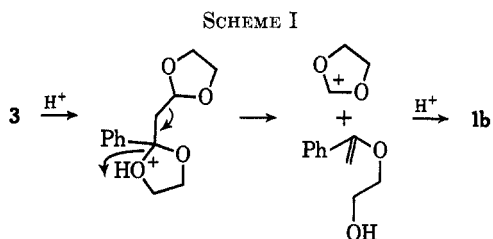
The sequence of steps finally employed for the synthesis of 1a is virtually identical with that used by Feugeas and Giusti for their synthesis of 2-ethynyl-2-methyl-1,3-dioxolane from 2-(1-bromoethyl)-2-methyl-1,3-dioxolane.² The only facet of our work worthy of mention is the preparation of 2-(1-bromoethyl)-2-phenyl-1,3-dioxolane (5). The analogous compound in the



French workers' series was prepared *via* ketalization of the appropriate α -bromo ketone, but in our case the requisite α -bromo ketone cannot be easily obtained.³ However, we have found that Eaton's conditions⁴ produce a good yield of 5 from 2-ethyl-2-phenyl-1,3-dioxolane.

When 1a was subjected to the conditions which converted 2 to 3 nmr analysis of the crude product revealed that no reaction had occurred.⁵ This fact and the observation that 1a is not seen during the conversion 2 \rightarrow 3 show that if 1a is ever formed during this conversion it is present in minute quantities, and if present it obviously does not react directly with *p*-toluenesulfonic acid-ethylene glycol to form 3. Consideration of these data and the fact that an intermediate with spectral properties strongly suggestive of 4 is observed during the conversion 2 \rightarrow 3 causes us to assume that 4 is the prime intermediate in this conversion.

The facile formation of 3 from 2 and the fact that 3 yields 1b when treated with anhydrous *p*-toluenesulfonic acid suggest the conversion 2 \rightarrow 1b proceeds at least in part *via* fragmentation of 3 (Scheme I). This frag-



mentation is similar to one discovered by Kraus (Scheme II).⁶

Our inability to isolate pure 4 has so far precluded experiments which would ascertain whether or not any product is formed *via* its fragmentation.

(2) C. Feugeas and G. Giusti, *C. R. Acad. Sci., Ser. C*, **264**, 1772 (1967).

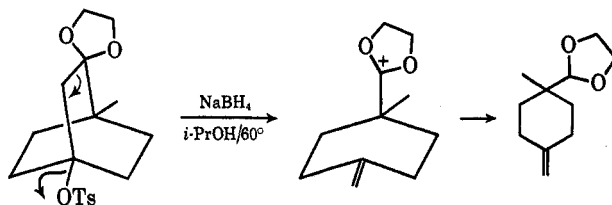
(3) F. Kröhnke and H. Timmler, *Chem. Ber.*, **69**, 614 (1936).

(4) P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2344 (1962). We acknowledge a fruitful discussion with Professor R. E. Lehr.

(5) The conditions must be strictly anhydrous since 1a is readily hydrolyzed to 2 in the presence of even trace quantities of hydronium ion.

(6) W. Kraus and C. Chassin, *Justus Liebigs Ann. Chem.*, **735**, 198 (1970).

SCHEME II



Experimental Section

Melting points were obtained on an Arthur H. Thomas Co. Unimelt apparatus and are uncorrected. Microanalyses were carried out by Chemalytics, Inc., Tempe, Ariz. Infrared spectra were obtained using a Beckman IR-8 recording spectrophotometer. Nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60 spectrometer. In all cases carbon tetrachloride was employed as solvent and tetramethylsilane (τ 0.00 ppm) as internal reference. Mass spectra (80 eV) were obtained by Professor R. E. Lehr, Mr. J. M. Wilson, and Mr. R. W. Allen using a Hitachi Perkin-Elmer Model RMU-7 double-focusing mass spectrometer equipped with a direct inlet system. Analytical scale thin layer chromatography (tlc) and preparative layer chromatography (plc) plates were prepared using silica gel PF-254 366 (E. Merck AG).

Unless otherwise noted the following standard work-up procedure was employed. The crude reaction mixture was poured into 100 ml of ether and extracted with three 30-ml portions of 10% potassium hydroxide and one 30-ml portion of saturated sodium chloride. After drying the organic phase with anhydrous magnesium sulfate, the solvent was removed at reduced pressure with the aid of a rotary evaporator and steam bath.

Propioloophenone (2).—The method of Bowden, Heilbron, Jones, and Weedon⁷ was used to prepare propioloophenone, mp 49–50° (lit.⁷ mp 50–51°).

2-Methyl-2-phenyl-1,3-dioxolane (1b) and 2-Ethyl-2-phenyl-1,3-dioxolane.—The method of Salmi, Tamminen, and Louhenkuru⁸ was used to prepare authentic samples of 2-methyl-2-phenyl-1,3-dioxolane, mp 58–59° (lit.⁸ mp 60–61°), and 2-ethyl-2-phenyl-1,3-dioxolane, bp 65° (1.8 mm) [lit.⁸ bp 87.7° (3 mm)].

2-(1-Bromoethyl)-2-phenyl-1,3-dioxolane (5).—A solution of 2-ethyl-2-phenyl-1,3-dioxolane (19.0 g, 0.11 mol) in 70 ml of tetrahydrofuran was cooled to 0° and 35.2 g (0.11 mol) of pyridinium bromide perbromide was added in one portion.⁴ The resulting mixture was stirred at 0° for 3 hr and 25° for 4 hr and filtered into a separatory funnel. The standard work-up procedure was used but the potassium hydroxide extractions were preceded by one with 40 ml of dilute sodium thiosulfate. Short-path distillation of the resulting oil afforded a forerun, bp 58–66° (0.2 mm), which was discarded and a main fraction, bp 79–89° (0.2 mm), which weighed 23.0 g (84%). It was sufficiently pure for use in the next step of the sequence. The analytical sample was a center cut from a second distillation (12-mm Vigreux column): bp 112° (0.7 mm); ir (neat) 9.27, 9.76, 14.18 μ ; nmr τ 2.36–2.85 (m, 5 H), 5.48–5.85 (q, partially superimposed on the OCH₂CH₂O multiplet), 5.72–6.40 (m), 8.44 (d, 3 H, *J* = 6.9 Hz). The mass spectrum of this material showed a parent doublet at *m/e* 256 and 258 and a base peak at *m/e* 149.

Anal. Calcd for C₁₁H₁₃O₂Br: C, 51.37; H, 5.11. Found: C, 51.52; H, 5.06.

2-Ethynyl-2-phenyl-1,3-dioxolane.—Potassium *tert*-butoxide (12.0 g, 0.11 mol, Alfa Inorganics-Ventron, Beverly, Mass.) was added to dimethyl sulfoxide (100 ml), and after the solution was cooled to 0° 20.9 g (0.08 mol) of 2-(1-bromoethyl)-2-phenyl-1,3-dioxolane was added over a 1.5-hr period. The mixture was stirred for 1.5 hr at 0° and 20 hr at 25°. Standard work-up procedure gave an oil, short-path distillation of which produced a liquid: bp 59–68° (0.3 mm); 13.5 g (95%); ir (neat) 9.39, 9.84, 14.29 μ ; nmr τ 2.42–2.92 (m, 5 H), 3.79–5.05 (m, 3 H), 5.92–6.42 (m, 4 H). The mass spectrum of this material showed a parent ion at *m/e* 176 and a base peak at *m/e* 149.

Anal. Calcd for C₁₁H₁₂O₂: C, 74.96; H, 6.87. Found: C, 75.12; H, 6.78.

(7) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(8) E. J. Salmi, U. Tamminen, and P. Louhenkuru, *Suom. Kemistilehti, B*, **20**, 1 (1947).

2-(1,2-Dibromoethyl)-2-phenyl-1,3-dioxolane.—2-Ethenyl-2-phenyl-1,3-dioxolane (17.2 g, 0.098 mol) was dissolved in 100 ml of carbon tetrachloride and cooled to 0°. Bromine was added dropwise until the color was no longer discharged. The standard work-up procedure was used but the potassium hydroxide extractions were preceded by one with 50 ml of dilute sodium thiosulfate. A slightly yellow solid resulted, mp 80–83°. Four crystallizations from methanol provided the analytical sample: white microprisms; mp 81.5–83°; ir (KBr) 8.23, 9.50, 10.03, 10.48, 14.22 μ ; nmr τ 2.37–2.82 (m, 5 H), 5.50–6.82 (m, 7 H). The mass spectrum of this material did not exhibit a parent ion. The base peak was at m/e 149 and there was a low intensity triplet at m/e 257, 259, 261.

Anal. Calcd for $C_{11}H_{12}O_2Br_2$: C, 39.31; H, 3.60. Found: C, 39.17; H, 3.58.

2-Ethynyl-2-phenyl-1,3-dioxolane (1a).—A suspension of sodamide in 150 ml of liquid ammonia was prepared from 10.6 g (0.46 g-atom) of sodium.⁹ To this stirred solution 27.2 g (0.081 mol) of 2-(1,2-dibromoethyl)-2-phenyl-1,3-dioxolane was added over 30 min (no solvent). After an additional 1.5 hr 21 g of ammonium chloride was added followed by 400 ml of ether. The yellow oil which remained after the standard work-up procedure was distilled, bp 92–96° (0.6 mm), giving 11.3 g (80%) of a colorless liquid. Silica gel plc (29% ether-hexane) gave the analytical sample: ir (neat) 3.03, 4.73, 9.32, 9.74 μ ; nmr τ 2.19–2.87 (m, 5 H), 5.70–6.24 (m, 4 H), 8.39 (s, 1 H). The mass spectrum of this material showed a parent ion at m/e 174 and base peak at m/e 97.

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.90; H, 5.90.

2-Methyl-2-phenyl-1,3-dioxolane (1b) from Propioloophenone (2).—*p*-Toluenesulfonic acid monohydrate (2.25 g, 12 mmol), 4 ml of ethylene glycol, and 50 ml of benzene were refluxed for 1 hr with azeotropic removal of water. This solution was cooled to room temperature and 1.44 g (11 mmol) of propioloophenone was added in one portion. Reflux was resumed for 16.5 hr after which the solution was worked up in the standard fashion. Sublimation [50–60° (2 mm)] of the resulting oil afforded 0.95 g (52%) of a white crystalline solid, mp 58–61° (lit.⁸ mp 60–61°). The infrared and nmr spectra obtained were identical with those of an authentic sample of 2-methyl-2-phenyl-1,3-dioxolane.

2-Phenyl-2,2'-methylenebis-1,3-dioxolane (3).—*p*-Toluenesulfonic acid monohydrate (0.025 g, 0.13 mmol), 4 ml of ethylene glycol, and 20 ml of benzene were refluxed for 10 min with azeotropic removal of water. The solution was cooled to room temperature and 0.63 g (4.8 mmol) of propioloophenone was added. The new mixture was refluxed for 4 hr with azeotropic removal of water and cooled to room temperature. Standard work-up gave 1.06 g of oil which appeared (nmr) to be a mixture of 2 and 1b (13:1). Trituration with ether-hexane gave 0.95 g (84%) of a white prismatic solid which melted at 53–54.5° after three crystallizations from ether-hexane: ir (KBr) 9.62, 13.99 μ ; nmr τ 2.46–2.93 (m, 5 H), 5.08–5.28 (t, 1 H, $J = 7.8$ Hz), 5.89–6.47 (m, 8 H), 7.72–7.85 (d, 2 H, $J = 7.8$ Hz). The mass spectrum of this material did not exhibit a parent ion. The base peak appeared at m/e 149. There were also sizable ions at m/e

73 and 105. The mass spectrum of a similar molecule is in the literature.¹⁰

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.17; H, 6.78.

Reaction of Propioloophenone (2) with 1 Equiv of Ethylene Glycol.—A mixture of 0.697 g (11 mmol) of ethylene glycol, 0.032 g (0.17 mmol) of *p*-toluenesulfonic acid monohydrate, and 20 ml of benzene was refluxed with azeotropic removal of water for 15 min. The mixture was cooled to room temperature and 1.47 g (11 mmol) of propioloophenone was added. This mixture was refluxed for 3 hr with azeotropic removal of water and cooled to room temperature. Standard work-up procedure gave 2.00 g of oil; nmr analysis indicated the presence of 2-phenyl-2,2'-methylenebis-1,3-dioxolane (3) and a second compound which exhibited a triplet (τ 4.56–4.78, $J = 8.1$ Hz) and doublet (τ 6.69–6.83, $J = 8.1$ Hz). Two bands resulted from plc (successive developments with 15, 28, and 52% ether-hexane). The material isolated from the band with the greatest R_f proved to be 2 (0.43 g, 30%). The material isolated from the second band was an oil (1.12 g) which exhibited the characteristic nmr peaks of 3 and the unknown doublet and triplet. Also, nmr integration revealed the phenyl and OCH_2CH_2O regions contained more protons than would result from 3 alone. The ir of this oil showed a carbonyl absorption at 5.84 μ . The spectral data strongly suggest that the third component of the mixture was 1-oxo-1-phenyl-3-(1,3-dioxolane)propane (4); based on this assumption the yields of the three compounds were as follows: 2 (30%), 3 (34%), and 4 (14%).

Attempted Reaction of 2-Ethynyl-2-phenyl-1,3-dioxolane (1a) with Ethylene Glycol.—*p*-Toluenesulfonic acid monohydrate (0.07 g, 0.37 mmol), ethylene glycol (0.07 g, 1.2 mmol), and 30 ml of benzene were refluxed with azeotropic removal of water for 15 min. This solution was cooled to room temperature and 0.10 g (0.59 mmol) of propioloophenone was added. The new mixture was refluxed for 4.3 hr with azeotropic removal of water and with a calcium chloride drying tube affixed to the condenser and then cooled to room temperature. Standard work-up procedure left 0.10 g of an oil. Nmr analysis showed this to be mainly 1a; the characteristic peaks of 1b, 3, and 4 were missing.

Reaction of 2-Phenyl-2,2'-methylenebis-1,3-dioxolane (3) with Equimolar *p*-Toluenesulfonic Acid.—*p*-Toluenesulfonic acid monohydrate (0.40 g, 2.1 mmol), 1.2 ml of ethylene glycol, and 20 ml of benzene were refluxed with azeotropic removal of water for 10 min. This solution was cooled to room temperature and 0.58 g (2.4 mmol) of 2-phenyl-2,2'-methylene bis-1,3-dioxolane was added. The new mixture was refluxed for 47 hr and cooled to room temperature. Standard work-up procedure gave 0.68 g of oil; sublimation [50–60° (2 mm)] afforded 0.14 g (35%) of a white crystalline solid, mp 58–61° (lit.⁸ mp 60–61°). The infrared and nmr spectra were identical with those of an authentic sample of 2-methyl-2-phenyl-1,3-dioxolane.

Registry No.—1a, 29568-62-5; 2, 3623-15-2; 3, 29568-64-7; 5, 29568-65-8; ethylene glycol, 107-21-1; 2-ethynyl-2-phenyl-1,3-dioxolane, 29568-66-9; 2-(1,2-dibromoethyl)-2-phenyl-1,3-dioxolane, 29568-67-0.

(9) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 1034.

(10) G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **34**, 3618 (1969).