Although this step has previously been proposed for comparable reactions,[27] experimental evidence for the occurrence of free radicals has previously been lacking.

Acknowledgment. Financial assistance from the Natural Sciences and Engineering Research Council of Canada is acknowledged. J.F.P.-B. is also thankful to the Spanish Ministry of Education and Science for the grant that made possible his participation in this project.

Registry No. Acrylic acid, 79-10-7; methacrylic acid, 79-41-4; crotonic acid, 3724-65-0; 3,3-dimethylacrylic acid, 541-47-9; cinnamic acid, 621-82-9; elaidic acid, 112-79-8; oleic acid, 112-80-1; methyltributylammonium permanganate, 82444-42-6; deuterium, 7782-39-0; propionic acid, 79-09-4; caproic acid, 142-62-1; valeric acid, 109-52-4; isobutyric acid, 79-31-2; butyric acid, 107-92-6; acetic acid, 64-19-7; benzoic acid, 65-85-0; *p*-chlorophenylacetic acid, 1878-66-6; 3-chloropropionic acid, 107-94-8; *m*-bromobenzoic acid, 585-76-2; *p*-nitrophenylacetic acid, 104-03-0; *m*-nitrobenzoic acid, 121-92-6; *o*-chlorobenzoic acid, 118-91-2; chloroacetic acid, 79-11-8; 2-chloropropionic acid, 598-78-7; dichloroacetic acid, 79-43-6; trichloroacetic acid, 76-03-9.

Supplementary Material Available: Spectrum of the product (Mn^{3+}), typical first-order plot for the oxidation of oleic acid by methyltributylammonium permanganate, Arrhenius plot for the oxidation of cinnamic acid by methyltributylammonium permanganate, Hammett plot for the oxidation of meta- and para-substituted cinnamic acids by methyltributylammonium permanganate, and tables of rate constants for the oxidation of 3,3-dimethylacrylic acid and crotonic acid by methyltributylammonium permanganate (6 pages). Ordering information is given on any current masthead page.

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Free Radicals in Organic Synthesis. A Novel Synthesis of Ethylene Glycol Based on Formaldehyde

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1,3-Dioxolane reacted with formaldehyde in the presence of free radical initiators to produce 2-(hydroxymethyl)-1,3-dioxolane in moderate yield. 2-(Hydroxymethyl)-1,3-dioxolane was catalytically hydrogenated to ethylene glycol.

Introduction

The use of free radical reactions for the formation of carbon–carbon bonds has been known for years[1–4] but has not been used extensively in organic synthesis except for special reactions such as free radical cyclizations.[5] Free radical reactions have, however, been used increasingly in recent years for the synthesis of organic molecules.[6–10]

Kollar reported in 1984 on the development of a novel route to ethylene glycol based on the free radical addition of methanol to formaldehyde.[11–15] Radicals are generated by the thermal decomposition of di-*tert*-butyl peroxide. *tert*-Butyl alcohol and acetone are produced as important byproducts.[16] The process is summarized in eq 1–4.

$$\mathrm{(CH_3)_3COOC(CH_3)_3 \rightarrow (CH_3)_3CO^{\bullet}} \tag{1}$$

$$\mathrm{(CH_3)_3CO^{\bullet} + CH_3OH \rightarrow (CH_3)_3COH + \dot{C}H_2OH} \tag{2}$$

$$\mathrm{\dot{C}H_2OH + CH_2{=}O \rightarrow HOCH_2CH_2O^{\bullet}} \tag{3}$$

$$\mathrm{CH_3OH + HOCH_2CH_2O^{\bullet} \rightarrow HOCH_2CH_2OH + \dot{C}H_2OH} \tag{4}$$

Because of the ease of reaction of formals under free radical generating conditions,[17–20] we investigated the reaction of 1,3-dioxolane (**1**) with formaldehyde under various conditions. This paper reports our initial work on the reaction of 1,3-dioxolane (**1**) with formaldehyde under free radical conditions. The major product, 2-(hydroxymethyl)-1,3-dioxolane (**2**), can be hydrogenated to ethylene glycol—an industrially important product.[21]

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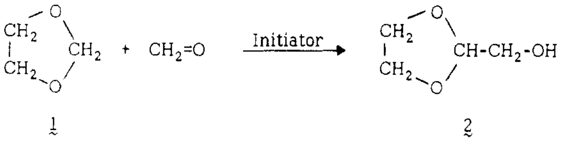
Table I. Reaction of 1,3-Dioxolane with Formalin

compound	area %	mass ion	abundnce	base peak
formaldehyde		30	50.8	29
water	30.6			
1,3-dioxolane (**1**)		74	4.3	73
1,3-dioxane (**8**)		88	6.2	87
formic acid		30	50.8	29
glycolaldehyde (**3**)	5.1			
ethylene glycol (**5**)	12.1	62	4.0	31
hydroxyethyl formate (**10**)	3.2	104	0.6	31
1,3-propanediol (**7**)	1.5	73	~0	31
2-(hydroxymethyl)-1,3-dioxolane (**2**)	15.8	104	0.4	73
4-(hydroxymethyl)-1,3-dioxolane (**11**)	trace			
hydroxypropyl formate (**6**)	1.66			
2-(hydroxymethyl)-1,3-dioxane (**12**)	5.8	118	~0	87
$\overline{O(CH_2)_2O}CH(CH_2O)_nH$ (n = 2–6) (**4**)	12.2			103

Results and Discussion

The reaction of **1** with formaldehyde in the presence of initiators such as di-*tert*-butyl peroxide or *tert*-butyl perbenzoate produced 2-(hydroxymethyl)-1,3-dioxolane (**2**) as the main product (eq 5). A variety of other products were also produced.



(5)

In an example, **1** (80 mL) was heated at 100–130 °C for 4 h with formalin (17 mL) and *tert*-butyl perbenzoate (3.0 mL). After most of the unreacted **1** was removed, a light yellow oil, weighing 19.1 g remained. This mixture was analyzed by GC/MS and GC/FTIR. The results are summarized in Table I.

The main product **2** was likely formed by a free radical chain process similar to the one proposed by Kollar.[11] An outline of the possible mechanism of formation of **2** as well as the other products detected in the reaction mixture is shown in Scheme I. Because of the sensitivity of the products as well as reactants to water in the system, the reaction of dioxolane with paraformaldehyde was also investigated.

The main products of the reaction when **1** (80 mL) was reacted with paraformaldehyde (10 g) and initiator (3.0 mL) under various conditions are shown in Table II. The selectivities to the products in this reaction were strongly temperature dependent. The selectivity to byproduct ethyl formate (**9**) could be reduced by conducting the reaction at a lower temperature. At 180 °C, ~33% selectivity to **9** was observed, whereas, at 75 °C, the selectivity dropped to ~3%. In general, the selectivity to **2** was also better at lower temperatures.

The addition of weak bases such as sodium and lithium carbonate to the reaction mixture did not improve results significantly. The addition of strong acids such as toluenesulfonic acid was detrimental. (Less than 10% selectivity to **2** + **4** was obtained under conditions where greater than 50% selectivities were usually observed.)

Table II. Reaction of 1,3-Dioxolane with Paraformaldehyde

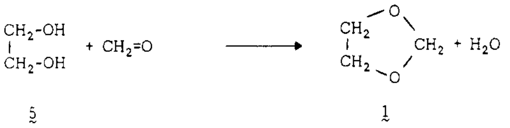
expt	time, h	temp, °C	initiator	selectivity, % 9	selectivity, % 2	selectivity, % 4
1	5	140	di-*tert*-butyl peroxide	32.3	24.2	8.14
2	3	160	di-*tert*-butyl peroxide	35.3	20.1	8.53
3	2	180	di-*tert*-butyl peroxide	33.2	18.0	7.72
4	6	100	*tert*-butyl perbenzoate	9.5	46.6	13.7
5	4	120	*tert*-butyl perbenzoate	12.4	41.9	15.0
6	3	140	*tert*-butyl perbenzoate	16.6	36.3	11.3
7	7	75	*tert*-butyl hydroperoxide/Co^{2+}	2.99	44.9	7.76
8	6	30	acetone/$h\nu$	<1	65.8	18.2

The photochemical reaction of **1** with formaldehyde using an acetone sensitizer produced a selectivity to **2** of 65% and a selectivity to **4** of 18%. The selectivity to **9** was reduced to less than 1%.

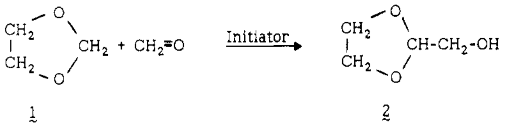
Pure **2** was isolated from a reaction mixture and hydrolyzed/reduced with Pd/C in a "one-pot" reaction to give ethylene glycol in 97.5% selectivity. Other catalysts were also found to be suitable for this reduction.

Conclusion. Free radical reaction of 1,3-dioxolane and formaldehyde afforded 2-(hydroxymethyl)-1,3-dioxolane **2** with a series of interesting byproducts.

Since hydrolysis of **2** and reduction gives good yields of ethylene glycol, the overall result is the production of ethylene glycol from formaldehyde and hydrogen (eq 6–10).



(6)



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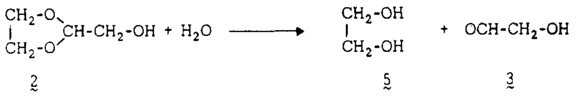
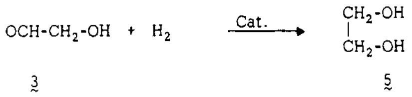
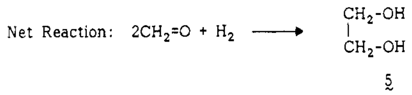


$$\begin{array}{l}CH_2\text{-}O\\ |\\ CH_2\text{-}O\end{array}\!\!\!>CH\text{-}CH_2\text{-}OH + H_2O \longrightarrow \begin{array}{l}CH_2\text{-}OH\\ |\\ CH_2\text{-}OH\end{array} + OCH\text{-}CH_2\text{-}OH \qquad (8)$$



$$OCH\text{-}CH_2\text{-}OH + H_2 \xrightarrow{\text{Cat.}} \begin{array}{l}CH_2\text{-}OH\\ |\\ CH_2\text{-}OH\end{array} \qquad (9)$$



$$\text{Net Reaction:}\quad 2CH_2{=}O + H_2 \longrightarrow \begin{array}{l}CH_2\text{-}OH\\ |\\ CH_2\text{-}OH\end{array} \qquad (10)$$

We plan to extend this reaction to other reactive substrates. For example, the reaction of ethers and alkyl aromatics with formaldehyde under free-radical generating conditions should produce useful primary alcohols.

Experimental Section

Chemicals. *tert*-Butyl peroxide, dioxolane, and *tert*-butyl perbenzoate were commercial products (>98% purity). All were used without further treatment.

Analytical. ^1H NMR spectra were recorded on a Varian EM-390 spectrometer. ^{13}C NMR spectra were recorded on a Bruker WP-80 spectrometer. The GC/FTIR work was done on a Digilab FTS 15E and the GC/MS work with a Hewlett-Packard 5790 mass-selective detector. Some analytical GLC was carried out with a Hewlett-Packard 5890 equipped with an 8 ft × $^1/_8$ in. Ni column with Poropak PS (80 × 100 mesh), He at 20 cm^3/min, progression 80–260 °C at 16 deg/min after a 4-min hold. A typical run follows: identification (retention time in minutes), water (1.81), methanol (5.53), ethanol (6.54), acetone (7.86), ethyl formate (8.05), *tert*-butyl alcohol (8.53), **1** (9.29), ethylene glycol (12.18), glycol esters (13.18), **2** (13.80), **4a** (18.01), **4b** (19.15).

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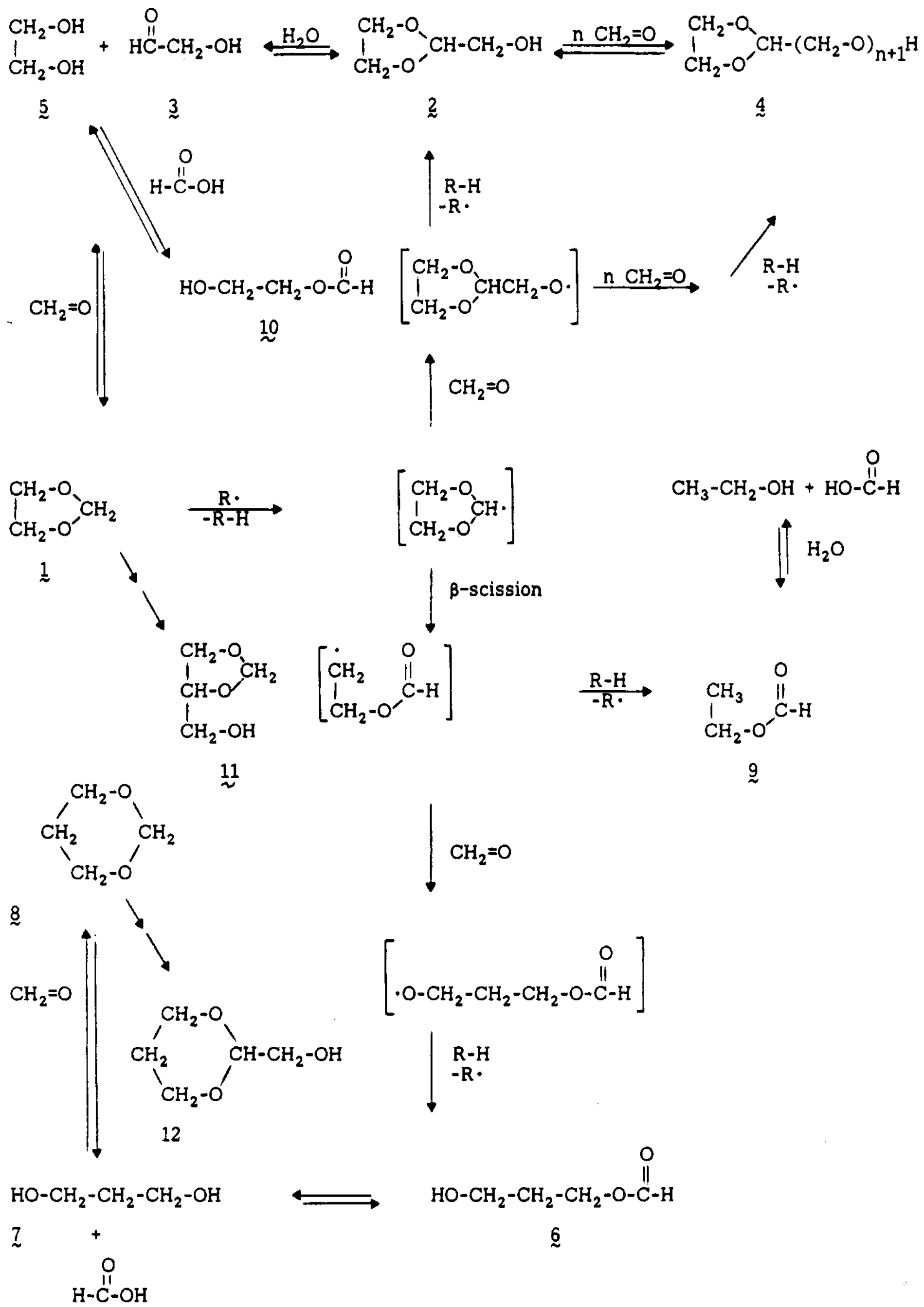
[21] Some of this work appears in a patent. Yeakey, E. L.; Sanderson, J. R. (Texaco) U.S. Patent 4 550 184, 1985. See also, Sanderson, J. R.; Yeakey, E. L.; Lin, J. J. (Texaco) U.S. Patent 4 554 364, 1985.

Scheme I. Reaction of 1,3-Dioxolane with Formalin



Identification of 2. Most of the dioxolane (from one of the reaction mixtures) was removed on a rotary evaporator and the remaining liquid distilled through a small (10-cm) Vigreux column. A clear liquid [bp 83–84 °C (15 mmHg)] was collected: ^{1}H NMR (90 MHz, neat) δ 3.91 (m, 4 H), 4.92 (t, 1 H), 3.53 (d, 2 H, J = 4 Hz); ^{13}C NMR (D_2O) δ 63 (CH_2), 66 (CH_2), 104 (CH); IR 3625, 2980, 2950, 2900, 1760, 1380, 1375, 1160, 1065, 860 cm^{-1}; mass spectrum, m/z (relative intensity) 27 (15.1), 28 (6.3), 29 (36.8), 31 (13.4), 43 (25.6), 44 (20.4), 45 (68.0), 57 (0.9), 73 (100.0), 103 (0.6).

Identification of 4a and 4b. The pot residue from the distillation of 2 was analyzed by GC and shown to be a mixture of mainly 2 and 4 with some ethylene glycol and formaldehyde. By ^{1}H NMR, the ratio of protons at δ 3.91 to the protons at δ 3.53 was 1:2. 4 was shown to be a mixture of higher homologues of 2. Two of these could be separated by GC/MS and GC/IR. The data are shown below. By subtracting out 2 as well as ethylene glycol and formaldehyde, we estimate that n in 4 ranges from 2 to 5.

4a (**n = 2**): mass spectrum, m/z (relative intensity) 27 (17.5), 28 (8.6), 29 (70.0), 31 (79.9), 43 (41.9), 44 (19.2), 45 (55.3), 57 (95.3), 73 (5.9), 103 (100.0), 133 (0.7); IR 3645, 2940, 2800, 1760, 1460, 1395, 1350, 1150, 1060, 860 cm^{-1}.

4b (**n = 3**): mass spectrum, m/z (relative intensity) 27 (14.1), 28 (9.2), 29 (68.6), 31 (72.2), 43 (37.4), 44 (28.0), 45 (47.3), 57 (100.0), 73 (3.1), 103 (99.2), 133 (0.3); IR 3650, 2940, 2895, 1760, 1460, 1375, 1350, 1150, 1060, 870 cm^{-1}.

Others. Other products were identified by comparison of their MS or FTIR spectra with those of the authentic materials.

Procedure (Thermal). Dioxolane, paraformaldehyde, and initiator were charged to a 300-cm^3 stainless steel autoclave equipped with a glass liner and Magne Drive stirrer. No special precautions were taken to exclude oxygen. The reaction mixture was heated to the desired temperature and held there for the required time. The times and temperature are given in Table II, experiments 1–7. (The pressure ranged from 40–200 psig depending on temperature.) At the end of the reaction, the mixture was cooled to ambient temperature, filtered from a small amount of formaldehyde and analyzed by GC, GC/FTIR, and/or GC/MS.

Procedure (Photochemical). A Pyrex photochemical reactor equipped with a water-cooled Pyrex immersion well was charged with dioxolane, formalin, and acetone. The mixture was irradiated with a 100-W Hanovia lamp at 30–35 °C for the required time and analyzed by GC. A representative example is shown in Table II, experiment 8.

Procedure (Reduction). **2** (10.3 g, >95% purity), distilled water (40 mL), and 5% Pd on C (2.0 g) were charged to a 100-cm^3 rocker autoclave and heated at 160 °C (2000 psig H_2) for 4 h. Analysis of the filtered reaction mixture showed 98.3% **2** conversion with 97.5% selectivity to ethylene glycol.

The above reaction was repeated except by using 2.0 g of 5% Pd on Al_2O_3. A 97.1% conversion of **2** was obtained with a 99.1% selectivity to ethylene glycol.

Registry No. **1**, 4421-14-1; **2**, 5694-68-8; **3**, 141-46-8; **4a**, 108665-17-4; **4b**, 108665-18-5; **5**, 107-21-1; **9**, 109-94-4; **10**, 628-35-3; **12**, 39239-93-5; formaldehyde, 50-00-0.

Control by Pyridine Nitrogen of the Dual-Channeled Triplet-State Di-π-methane Photorearrangement of 5,8-Dihydro-5,8-methanoquinoline Systems

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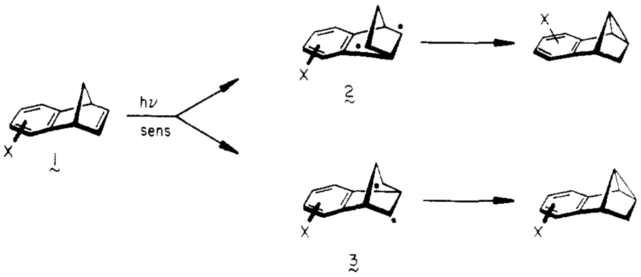
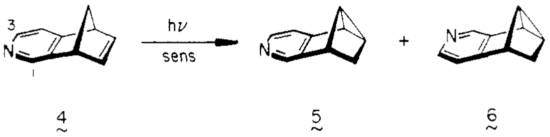
A series of five 5,8-dihydro-5,8-methanoquinolines has been synthesized and the triplet-state photoisomerization of these compounds investigated. In the case of the parent heterocycle, a 60:40 distribution of the two possible photoisomers was observed, with the major product arising by migration of the carbon atom ortho to nitrogen. Adoption of this pathway is notably enhanced (to the 83% level) when a chlorine is positioned at C-2 and becomes exclusive in the 2-methoxy example. The presence of a 4-chloro group reverses this trend (33:67), and the effect persists in the 4-methoxy example (25:75). The various regioselectivities are shown to conform to expectations which have their basis in molecular orbital theory.

In contrast to acyclic 1,4-dienes, which are so constructed as to engage in a single initial photoactivated "bridging step",[2] benzonorbornadienes have the latent ability to engage in two competitive excited-state 1,2-aryl-shift processes (viz., **1** → **2** and **1** → **3**).[3] This dual-channel feature prompted us some time ago to undertake an extensive investigation of the controlling influence of substituents bonded to either of the two possible aryl sites,[4] to an olefinic center,[5] and to the bridgehead positions (singly[6] and doubly functionalized[7]). Internal competition experiments between various aryl/vinyl,[5b,c] bridgehead/vinyl,[8] and aryl/bridgehead substituent pairs[9] have also been performed, and the observed regiocontrol has proven highly revealing of detailed mechanism.[6-9]



More recently, we reported on the triplet-sensitized photorearrangement of several 5,8-dihydro-5,8-methanoisoquinolines,[10] the first heteroaromatics to be examined in this manner. For the parent heterocycle **4**, the ring nitrogen atom was found to exert a directing influence favoring migration of C_{para} (75% of **5**; 25% of **6**). Attachment of chloro and methoxy groups at C-3 proved synergistic to the C_{para} 1,2-shift as expected. When the methoxy substituent was positioned at C-1 where it could operate in an antagonist fashion against nitrogen, OCH_3 totally controlled the regiochemical course of the di-π-methane rearrangement.[10]



In view of these developments, the scope of our investigations has now been expanded to include the isomeric 5,8-dihydro-5,8-methanoquinoline (**7**) and a number of its derivatives (**8** and **9**). Whereas the substitution plan in **4** is one that requires the sp^2-hybridized carbons positioned meta and para to the nitrogen center to vie for control of the rebonding pathways, the situation in **7** causes attention to be paid specifically to the C_{ortho}/C_{meta} pair. The ortho

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