(m, 2 H), 5.40–6.00 (m, 1 H), 6.67–7.40 (m, 5 H). Anal. Calcd for $C_{17}H_{22}O$: C, 84.24; H, 9.14. Found: C, 84.31; H, 9.23.

Palladium-Catalyzed Reaction of 17 in the Presence of NaH in *t*-BuOH. A mixture of 17 (420 mg, 2 mmol), NaH (100 mG), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), and PPh_3 (104 mg, 0.4 mmol) in *t*-BuOH (20 mL) was stirred for 4 h at 50 °C. After the reaction was complete (TLC and GLC analyses), the reaction mixture was neutralized and extracted with CH_2Cl_2. Then pure 18 (169 mg, 51%) was isolated by column chromatography on silica gel.

General Procedure for the Palladium-Catalyzed Decarboxylation–Allylation of α-Substituted Allyl Cyanoacetates, Malonates, and Nitroacetate (Table II). A solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (26 mg, 0.05 mmol) an dppe (40 mg, 0.1 mmol) in dry DMF (3 mL) was stirred for 10 min at 20–25 °C under argon. To this solution, a solution of allyl ester (1 mmol) in dry DMF (0.5 mL) was added, and the resultant solution was stirred under argon. After the reaction was complete (TLC and/or GLC anaylses), the allylated product was isolated by column chromatography on silica gel.

Allyl 1-allylcyclohexanecarboxylate (48): ^1H NMR ($CDCl_3$, 90 MHz) δ 1.00–1.78 (m, 10 H), 2.22 (d, J = 12 Hz, 2 H, 4.58 (d, J = 5.4 Hz, 2 H), 5.00–5.42 (m, 4 H), 5.46–6.18 (m, 2 H); IR (neat) 2980, 1730, 1640, 1450, 990, 930 cm^{-1}.

Methyl 1-allylcyclohexanecarboxylate (51): ^1H NMR (CCl_4, 60 MHz) δ 0.70–2.00 (m, 10 H), 2.11 (d, J = 7 Hz, 2 H), 3.52 (s, 3 H), 4.60–5.00 (m, 1 H), 5.00–5.60 (m, 1 H); IR (neat) 2900, 2850, 1725, 1640, 1450, 1200, 1140 cm^{-1}.

Allyl 2-allylhexenoate (53): ^1H NMR ($CDCl_3$, 90 MHz) δ 0.88 (t, J = 5.7 Hz, 3 H), 1.04–1.80 (m, 6 H), 2.00–2.60 (m, 3 H), 4.76 (d, J = 6.5 Hz, 2 H), 4.90–5.44 (m, 4 H), 5.44–6.12 (m, 2 H); IR (neat) 3180, 2940, 1730, 1640, 1450, 995, 920 cm^{-1}.

5-Allyl-5-cyanononane (56): ^1H NMR ($CDCl_3$, 90 MHz) δ 1.00–1.78 (m, 10 H), 2.22 (d, J = 12.0 Hz, 2 H), 4.58 (d, J = 5.4 Hz, 2 H), 5.00–5.42 (m, 4 H), 5.46–6.18 (m, 2 H); IR (neat) 2980, 1730, 1640, 1450, 990, 930 cm^{-1}.

4-Cyano-1-octene (59): ^1H NMR ($CDCl_3$, 90 MHz) δ 0.70–1.10 (m, 3 H), 1.10–1.80 (m, 6 H), 2.10–2.70 (m, 3 H), 5.12 (d, J = 17 Hz, 2 H), 5.48–6.10 (m, 1 H); IR (neat) 3080, 2950, 2240, 1640, 1460, 990, 920 cm^{-1}.

4-Allyl-4-nitroheptane (62): ^1H NMR ($CDCl_3$, 90 MHz) δ 0.80–1.48 (m, 10 H), 1.72–2.04 (m, 4 H), 2.66 (d, J = 7.2 Hz, 2 H), 4.96–5.35 (m, 2 H), 5.32–5.88 (m, 1 H); IR (neat) 3070, 2960, 1640, 1550, 1460, 990, 920 cm^{-1}.

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Alkylation of Pentaerythritol by Phase-Transfer Catalysis. 3. Influence of the Tetrahedral Structure of Pentaerythritol on the Rate and Selectivity of the Phase-Transfer-Catalyzed Reaction

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The rates and selectivity of the phase-transfer-catalyzed etherification of pentaerythritol [2,2-bis(hydroxymethyl)-1,3-propanediol] and ethylenetetramethanol [2,3-bis(hydroxymethyl)-2-butene-1,4-diol] have been compared under similar phase-transfer alkylation conditions. The results described herein clearly indicate that the tetrahedral structure of pentaerythritol explains the successful alkylation results pointed out in previous papers.

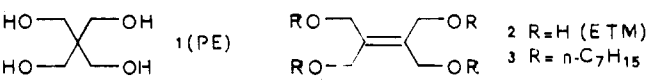
In our previous papers, we have discussed the selectivity of the alkylation of pentaerythritol[1] (PE) and provided an explanation for the formation of a mixture of tri- and tetraethers. The role of the solubility of the phase-transfer catalyst and the excess of sodium hydroxide, which are the key factors for the completion of this PTC reaction, were also reported.[2]

However, no explanation has been given why such a hydrophilic polyalcohol reacts so easily and so rapidly under phase-transfer conditions.[3]

Recently, we have had an opportunity[4] to develop a new synthetic route to the 2,3-bis(hydroxymethyl)-2-butene-1,4-diol (2) (ETM), a tetraalcohol with four primary hydroxyl functions but without the tetrahedral spatial conformation of the CH_2OH groups of PE (Chart I).

In the present work, we have compared the selectivity and the rates of formation of *n*-heptyl ethers for these two

Chart I



polyalcohols under PTC conditions.

Results and Discussion

Alkylation of **2** by *n*-heptyl bromide was accomplished with a large excess of sodium hydroxide (80 equiv) and tetrabutylammonium bromide as the catalyst. By monitoring the reaction by GC, it was first observed that the reaction was very slow. After 2 h, the organic phase was composed of only 5% of the tetra-*n*-heptyl ether of ETM (**3**) and 34% of di-*n*-heptyl ether (Figure 1).

The presence of di-*n*-heptyl ether is fully consistent with the hydrolysis of the halide by the hydroxide anions in the organic phase.[5] The newly formed 1-heptanol is then transformed into the symmetrical ether by a classical PTC process.[6]

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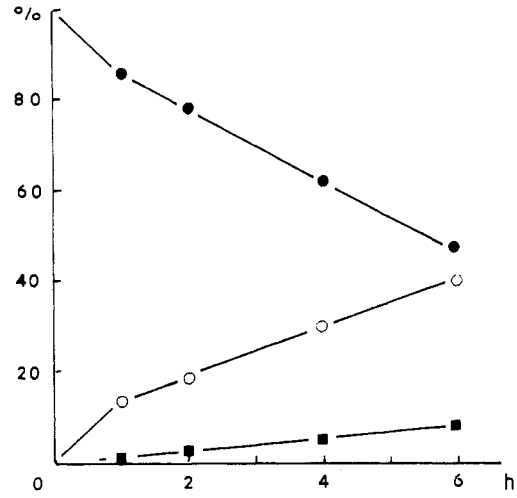


Figure 1. Alkylation of ETM (2): relative concentration of n-$C_7H_{15}Br$ (●), di-n-heptyl ether (○), and tetraether of ETM (■).

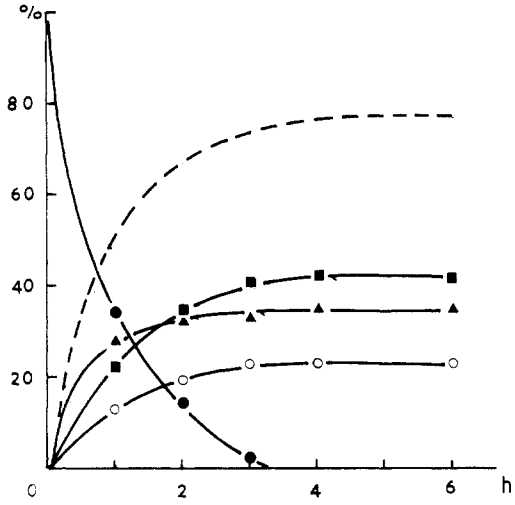


Figure 2. Alkylation of PE (1): relative concentration of n-$C_7H_{15}Br$ (●), di-n-heptyl ether ($C_7H_{15}OC_7H_{15}$) (○), triether of PE (△), and tetraether of PE (■) (dotted line: total triether + tetraether).

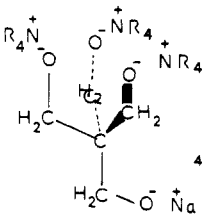
The extraction of the hydroxide anion by ammonium is nevertheless difficult because of its solubility and its small extraction constant k (eq 1).[9]

$$[NR_4Br]_{org} + [OH^-]_{aq} \overset{k}{\rightleftharpoons} [NR_4OH]_{org} + [Br^-]_{aq} \quad (1)$$

Many arguments have been advanced against this extraction scheme.[7] The alkoxide anions of alcohols are more lipophilic than the hydroxide ions and would be therefore extracted preferentially. The success of a PTC reaction depends on this preferential extraction.[8] Thus it was assumed that the rate of formation or extraction of reactive ion pairs consisting of an alkoxide of **2** with tetrabutylammonium cations was very slow.

In contrast with PE, we observed that the PTC alkylation of ETM gave only the tetraether **3** in a low yield. When **2** was treated with n-heptyl bromide in a 1:4 molar ratio, the pure tetraether **3** was isolated in 10% yield.

Chart II



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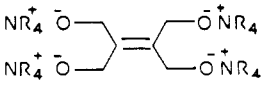

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Further addition of n-$C_7H_{15}Br$ after periods of 8 h may increase the total yield (40%). In the case of PE, under the same reaction conditions, after 2 h, the mixture of tri- and tetraethers represents 45% of the organic phase and di-n-heptyl ether) only 14% (Figure 2). At the end of the reaction the yield of isolated ethers is 64% (75.5% with further addition of n-$C_7H_{15}Br$ after 8 h).

These observations lead to the suggestion that the difference between the rates and selectivity of alkylation of **1** and **2** lies in the possibility of transport of the tris(tetrabutylammonium) PE salt (**4**) into the organic phase, whereas the transport of **2** in the form of a reactive ion pair with the tetrabutylammonium cation requires the formation of the tetrakis(tetrabutylammonium) ETM salt (**5**).

The tetrahedral structure of PE seems to be the determining factor in the facile formation at the interface of the tris(tetrabutylammonium) PE salt (**4**), through a "tripod-like" conformation of three C-CH_2O^- bonds (Chart II).

The bis(tetrabutylammonium) salts of PE and ETM remain in the aqueous phase, with the two lipophilic tetrabutylammonium groups near the interphase and the two hydrophilic sodium groups directed toward the aqueous phase. The etherification of alkoxide groups may then occur only after transport of the polyalcohol in the organic phase; the conversion of the third alkoxide group from the sodium to the ammonium form is then a prerequisite to the completion of the reaction. The rate of this cation exchange will depend directly on the ability of this third alkoxide to be near the interphase (TBAB is only present in the organic phase). The tetrahedral structure of PE allows this if one considers the possible, facile, rotation of one of the C-$CH_2O^-Na^+$ bond, drawing the third alkoxide group near the interphase in the favored "tripod-like" conformation. Due to the relative flat conformation of ETM, the same procedure (exchange of the third cation at the interphase) requires the 90° rotation of the plane of the double bond and therefore the concomitant displacement toward the interphase of two hydrophilic sodium alkoxide groups. In the same way, glycerol led to the triheptyl ether (20%) and threitol or α-methyl glucoside to the tetraether (5–15%) without contamination respectively of the diether or triether. As for ETM, the formation of the reactive tetrabutylammonium–alkoxide ion pairs are difficult to attain due to the lack of the tetrahedral conformation; this in turn is reflected in a low yield etherification.

It is important to note that in these three cases the etherification of the secondary hydroxyl functions occurs easily. In fact, this reaction is difficult for steric reasons, but the rate of the extraction process is so slowed that the concentration of the reactive ammonium salt of the polyalcohol in the organic phase is very low. This organic phase is then almost exclusively composed of heptyl bromide and TBAB, thus making possible the etherification of the secondary hydroxyl group.

Except for PE and some polyols with a tetrahedral structure such as trimethylolpropane, one can therefore state that the Dehmlows' remark about PTC etherification:

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(7) See ref 3, pp 29–31. Makosza, M. *Pure Appl. Chem.* **1975**, *43*, 439. Starks, C. M.; Liotta, C. *Phase Transfer Catalysis Principles and Techniques*; Academic Press: New York, 1978; p 173.
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"water soluble compounds cannot react" (or more accurately: can react but in a low yield) remains valid. In conclusion the polyalcohols not having the tetrahedral conformation fail to react because the rate of hydrolysis of the halide is faster than the rate of polyol alkoxide extraction in the organic phase. We are now in the process of extending the scope of this direct PTC etherification to most of the carbohydrates.[10]

Experimental Section

Gas chromatography was performed with a Delsi IGC 120 FL Model, the column used was 3% SP 2100 on 120–140 mesh, Chromosorb G, 1.50 m. Liquid chromatography was performed on silica gel 60 (Merck, 0.063–0.200 mm) on a 15 × 150 mm column. PE and TBAB (Fluka) D,L-threitol (Aldrich), and α-methyl glucoside (Janssen) were dried before use (60 °C under reduced pressure).

Preparation of ETM (2). The tetraalcohol **2** was prepared by the previously[4] described $S_{RN}1$ reaction of 2,2-dimethyl-5-(hydroxymethyl)-5-nitro-1,3-dioxane with 2,2-dimethyl-5,5-dinitro-1,3-dioxane under basic conditions, elimination of the two nitro groups by Na_2S, and cleavage of the two acetals by a sulfonic acid resin.

Alkylation of ETM (2). The tetraalcohol **2** (0.58 g, 3.90 mmol) was added to a freshly prepared solution of NaOH (12.56 g, 314 mmol) in H_2O (12.6 mL). The mixture was stirred at 80 °C for 1 h; TBAB (0.5 g, 1.57 mmol) and *n*-heptyl bromide (2.81 g, 15.7 mmol) were added. The reaction mixture was then stirred 8 h at 80 °C. Water (15 mL) and diethyl ether (20 mL) were added, and the diethyl ether layer was separated, washed with water (3 × 10 mL), and dried. Evaporation gave an oil from which di-*n*-heptyl ether was distilled (Kugelrohr, 90 °C, 0.6 mmHg). The residue was purified by LC (silica gel); elution with pentane (200 mL) made it possible to remove the last small amount of di-*n*-heptyl ether, and elution with pentane–ether (3:1) (250 mL) afforded 0.202 g of the tetraheptyl ether **3** as a pale yellow oil (yield 9.6%): IR (KBr) 3000–2850, 1480, 1100 cm^{-1}. Anal. Calcd for $C_{34}H_{68}O_4$: C, 75.50; H, 12.67. Found: C, 75.56; H, 12.60.

In a second experiment under the same experimental conditions, 2.81 g of *n*-$C_7H_{15}Br$ was added after 8 h and the reaction was continued for an additional 8 h: 0.587 g, 27.9%.

Alkylation of PE (1). PE (0.53 g, 3.90 mmol) was alkylated in the same way as **2** and afforded, after the same workup and LC, a mixture of tri- (45% GC) and tetraethers (55% GC) (1.185 g) (64%, isolated). An additional amount (2.8 g) of *n*-$C_7H_{15}Br$ after 8 h led to 1.410 g (yield 75.5%) of ethers (tri, 32%; tetra, 68%). GC-monitored experiments were carried out under the same experimental conditions as described above. Each aliquot was processed in the manner described previously.[1]

Alkylation of Glycerol. Glycerol (0.46 g, 5 mmol) was alkylated in the same way as **2** (NaOH, 12 g, 300 mmol; H_2O, 12 mL; TBAB, 0.5 g, 1.5 mmol; $C_7H_{15}Br$, 2.7 g, 15 mmol). After purification (LC) the triheptyl ether was obtained (0.36 g, 0.93 mmol): yield 20%. Anal. Calcd for $C_{24}H_{50}O_3$: C, 74.55; H, 13.03. Found: C, 74.61; H, 13.05.

Alkylation of D,L-Threitol. The above procedure was used (threitol, 0.61 g, 5 mmol; NaOH, 16 g, 400 mmol; H_2O, 16 mL; TBAB, 0.65 g, 20 mmol; *n*-$C_7H_{15}Br$, 3.6 g, 20 mmol). After 8 h, an additional 3.6 g of *n*-$C_7H_{15}Br$ was added. After purification, the tetraether (0.385 g, 0.75 mmol) was obtained: yield 15%. Anal. Calcd for $C_{32}H_{66}O_4$: C, 74.65; H, 12.92. Found: C, 74.71; H, 12.90.

Alkylation of α-methyl glucoside (α-methyl glucoside, 0.97 g, 5 mmol; tetraether, 0.415 g, 0.70 mmol): yield 14%. Anal. Calcd for $C_{35}H_{76}O_6$: C, 70.89; H, 12.92. Found: C, 70.96; H, 12.87.

Registry No. **1**, 115-77-5; **1** (triheptyl ether), 97431-23-7; **1** (tetraheptyl ether), 97431-24-8; **2**, 54902-90-8; **3**, 108451-65-6; glycerol, 56-81-5; D,L-threitol, 6968-16-7; α-methyl glucoside, 97-30-3; *n*-heptyl bromide, 629-04-9; glycerol triheptyl ether, 108418-30-0; D,L-threitol tetraheptyl ether, 108451-66-7; α-methyl glucoside tetraheptyl ether, 108451-67-8.

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Existence and Reactivity of Bicyclic Annulenones. 2. Bicyclo[3.3.0]octa-1(5),3,7-triene-2,6-dione

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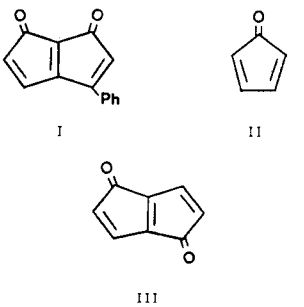
Evidence is presented that demonstrates the existence of free bicyclo[3.3.0]octa-1(5),3,7-triene-2,6-dione, which through an elimination process has been generated from an insoluble polymeric precursor. The diketone can act either as a diene or as a dienophile in pericyclic reactions.

A study of annulenones with fully unsaturated pentalenic structures was carried out by us, thus showing the existence and reactivity of 4-phenylbicyclo[3.3.0]octa-1-(5),3,6-triene-2,8-dione (I)[1] (Chart I). It was an elusive ketone with reactivity different from that of cyclopentadienone (II).[2] Since I was able to act as a diene, in Diels–Alder reactions, its behavior as a dienophile was never detected. Now we report the generation and reactivity of another unstable pentalenic diketone different from I in the relative position and orientation of its carbonyl groups: bicyclo[3.3.0]octa-1(5),3,7-triene-2,6-dione (III). For this purpose, we attempted first to prepare an adequate precursor able to yield III by an elimination reaction. This precursor was the polymeric sulfonate of 1-hydroxybicyclo[3.3.0]octa-4,7-diene-2,6-dione (VI, Scheme I).

Chart I



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