H), 2.9 (br s, 1 H), 2.74 (t, 2 H, J = 5.5).

Methyl 2-Diazo-5-hydroxy-3-oxopentanoate (38). The diazo transfer reaction was performed on **37** in the standard manner to give **38** in 77% yield after purification by column chromatography on silica gel (CH_2Cl_2/EtOAc, 9/1): IR ($CHCl_3$) 3400–3600, 2960, 2140, 1720 cm^{-1}; ^1H NMR δ 3.92 (br m, 2 H), 3.85 (s, 3 H), 3.11 (t, 2 H, J = 5.5), 2.9 (br s, 1 H).

2-(Methoxycarbonyl)-3-oxotetrahydrofuran (39). The carbenoid insertion reaction was performed with 1.5 mol % of $Rh_2(OAc)_4$ as described above to give **39** in quantitative yield: IR ($CHCl_3$) 2960, 1740 cm^{-1}; ^1H NMR δ 4.3–4.6 (m, 3 H), 3.78 (s, 3 H), 2.59 (t, 2 H, J = 7.8); mass spectrum for $C_6H_8O_4$, calcd m/e 144.0423, found m/e 144.0420.

Ethyl 5-(*S*-trityl)-3-oxopentanoate (46) was prepared by the general procedure for synthesizing β-keto esters. The crude product was pure enough to use in the next reaction; for analysis the material was chromatographed (hexanes/EtOAc, 1/1): 88% yield; mp 97–98 °C; IR ($CDCl_3$) 2890, 1730, 1710 cm^{-1}; ^1H NMR δ 7.48–7.2 (m, 15 H), 4.15 (q, 2 H, J = 7.2), 3.28 (s, 2 H), 2.43 (m, 4 H), 1.25 (t, 3 H, J = 7.1). Anal. Calcd for $C_{26}H_{26}O_3S$: C, 74.6; H, 6.3. Found: C, 75.0; H, 6.2.

Bis(ethyl 3-oxo-5-mercaptopentanoate) (43). To **46** (2.0 g, 4.78 mmol) in CH_2Cl_2/EtOH (2/1, 30 mL) was added iodine (2.7 g, 10.6 mmol). The solution was stirred at room temperature for 40 min and then diluted with saturated $NaHSO_3$ and extracted with ether. The ether solution was dried (Na_2SO_4), evaporated, and chromatographed on silica gel (hexanes/EtOAc, 7/3). Isolation of the lowest R_f spot gave **43** as a yellow mobile oil (627 mg, 75%): IR ($CDCl_3$) 2980, 1735, 1715 cm^{-1}; ^1H NMR δ 4.16 (q, 4 H, J = 7.1), 3.46 (s, 4 H), 2.96 (t, 4 H, J = 6.6), 2.85 (t, 4 H, J = 6.6), 1.25 (t, 6 H, J = 7.1). Anal. Calcd for $C_{14}H_{22}O_6S_2$: C, 48.0; H, 6.3. Found: C, 47.9; H, 6.3.

Bis(ethyl 2-diazo-3-oxo-5-mercaptopentanoate) (47) was prepared by the general procedure for diazo transfer reactions. The crude product was chromatographed twice (hexanes/EtOAc, 7/3) to give **47** as a yellow oil in 78% yield: IR ($CDCl_3$) 2980, 2140, 1705, 1640 cm^{-1}; ^1H NMR δ 4.26 (q, 4 H, J = 7.1), 3.23 (t, 4 H, J = 7.1), 2.92 (t, 4 H, J = 7.1), 1.28 (t, 6 H, J = 7.1).

Ethyl 2-Diazo-3-oxo-5-mercaptopentanoate (48). To **47** (514 mg, 1.28 mmol) dissolved in acetonitrile (2 mL) and aqueous potassium carbonate (0.5 mL, 0.2 M) was added dithioerythritol (395 mg, 2.56 mmol). The solution was stirred at room temperature for 15 min and then added to an ether/water mixture. The aqueous layer was extracted several times with ether, and then the organics were dried (Na_2SO_4) and evaporated to give an oil. Chromatography on silica gel (hexanes/EtOAc, 7/3) led to isolation of the material with the highest R_f as a light yellow oil: 305 mg (59%); IR ($CDCl_3$) 2980, 2135, 1708, 1640 cm^{-1}; ^1H NMR δ 4.31 (q, 2 H, J = 7.1), 3.20 (t, 2 H, J = 6.7), 2.79 (m, 2 H), 1.69 (t, 1 H, J = 8.4), 1.34 (t, 3 H, J = 7.1).

2-(Ethoxycarbonyl)-3-oxotetrahydrothiophene (49) was prepared by the general procedure for $Rh_2(OAc)_4$-catalyzed X–H carbenoid insertions. The solution was refluxed for 1 h, with 1.5 mol % of $Rh_2(OAc)_4$ in benzene, concentrated in vacuo, dissolved in CH_2Cl_2, and then filtered through silica gel to remove the red rhodium residues. The oil obtained on evaporation was Kugelrohr distilled (50 °C (~0.5 mm)) to give **49** as a colorless oil in 73% yield: IR (CH_2Cl_2) 2960, 1740, 1720 cm^{-1}; ^1H NMR δ 4.23 (m, 2 H), 4.01 (s, 1 H), 3.33 (m, 1 H), 3.08 (m, 1 H), 2.90 (m, 1 H), 2.67 (m, 1 H), 1.30 (t, 3 H, J = 7.2); ^{13}C NMR DEPT δ 62.3 (i), 52.1, 38.8 (i), 25.4 (i), 14.1; mass spectrum, m/e 174 (M^+, 56.65). Anal. Calcd for $C_7H_{10}O_3S$: C, 48.3; H, 5.8. Found: C, 48.4; H, 5.9.

Acknowledgment. We thank John F. O'Connell for conducting the NMR experiments on the Bruker AM 500 spectrometer.

Registry No. **6a**, 56-40-6; **6b**, 107-95-9; **6c**, 56-12-2; **6d**, 660-88-8; **7a**, 1138-80-3; **7b**, 2304-94-1; **7c**, 5105-78-2; **7d**, 23135-50-4; **8a**, 82961-77-1; **8a** (imidazolide), 99017-59-1; **8b**, 99017-63-7; **8b** (imidazolide), 99017-60-4; **8c**, 84446-29-7; **8c** (imidazolide), 99017-61-5; **8d**, 99017-64-8; **8d** (imidazolide), 99017-62-6; **9a**, 99017-65-9; **9b**, 99017-66-0; **9c**, 99017-67-1; **9d**, 99017-69-3; **10**, 99017-68-2; **16**, 99017-70-6; **17**, 99017-88-6; **19**, 92249-27-9; **20**, 99017-71-7; **21**, 99017-72-8; **22**, 99017-73-9; **24**, 29689-63-2; **25**, 99017-74-0; **28**, 77987-49-6; **29**, 99017-75-1; **30**, 99017-76-2; **32**, 99017-77-3; **33**, 99017-78-4; **34**, 99017-79-5; **36**, 99017-80-8; **37**, 99017-81-9; **38**, 99017-82-0; **39**, 99017-83-1; **40**, 107-96-0; **43**, 99017-85-3; **45**, 27144-18-9; **46**, 99017-84-2; **47**, 99017-86-4; **48**, 99017-87-5; **49**, 80278-79-1; $MeOCOCH_2CO_2H$, 16695-14-0; $EtOCOCH_2CO_2H$, 1071-46-1; (MeOCOCHCOO)Mg, 57907-72-9; diketene, 674-82-8.

Phase-Transfer Catalysis by Poly(ethylene glycol)s of β-Thioethyl Chloride Reactions

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Neighboring sulfur participation is a facile process for β-thioethyl derivatives. In the present work we examine the ability of phase-transfer catalysis by poly(ethylene glycol)s to make direct substitution, elimination, and oxidation competitive with neighboring sulfur participation for reaction of mustard chlorohydrin (1).

There has been much recent interest in the use of poly(ethylene glycol) (PEG) and its derivatives as phase-transfer agents.[1-8] In the present work we describe our use of these agents for catalysis of reactions of β-thioalkyl chlorides. These processes are of interest because of the difficulty in achieving reactions other than neighboring sulfur assisted (k_Δ) displacement in ionizing media. Thus we have shown that neighboring group participation by sulfur (and accompanying carbon scrambling) is much more facile than direct solvolytic displacement (a k_s process).[9] This inertness toward direct nucleophilic substitution is especially interesting in view of the facility with

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which solvolytic displacement occurs on other primary derivatives; e.g., it is estimated that nucleophilic solvent assistance provides a kinetic factor of approximately 10^8 for primary solvolyses.[10] Similarly, elimination is also a facile process for primary chlorides; yet it is not observed even at pH 10 for mustard chlorohydrin (1) or mustard gas (2).[11] Thus sulfur participation is so enormously facile,

$$\underset{\mathbf{1}}{HOCH_2CH_2SCH_2CH_2Cl} \qquad \underset{\mathbf{2}}{S(CH_2CH_2Cl)_2}$$

$$\underset{\mathbf{3}}{CH_3SCH_2CH_2Cl}$$

the quite powerful k_s and elimination processes are slow by comparison.[12] The goal of the present work is to determine if phase-transfer catalysis with PEG or PEG–alkyl ethers can produce reactions of β-thioalkyl chlorides which are competitive with the k_Δ process usually observed. This possibility seemed promising since, as explained below, the use of relatively nonpolar organic phases should slow the k_Δ process.

We have focused our attention on four reactions, all catalyzed by PEG or the nonylphenyl ether of PEG (R-PEG); these reactions are as follows: (1) substitution by acetate (benzene–solid acetate system); (2) alkylation by phenylacetonitrile (nitrile as one phase, water the other); (3) elimination (benzene/aqueous potassium hydroxide system); (4) sodium hypochlorite oxidation (benzene/water system). We have examined the efficacy of R-PEG for all these reactions because of its enhanced solubility in the benzene phase used in three of our four reactions; PEG itself greatly prefers the water phase in dilute solution[4] but nonetheless can be effective, especially if the aqueous salt layer is concentrated.[5]

Results and Discussion

In our recent work on hydrolysis of 1 we concluded that the reaction proceeded by neighboring sulfur participation.[9] As noted above, our present interest is to examine the ability of powerful nucleophiles and bases to compete with neighboring sulfur participation. An effective approach to greatly increasing nucleophilicity is to use a phase-transfer agent to dissolve an anionic nucleophile in a poorly solvating nonpolar solvent. For example, the normally weak nucleophile acetate becomes a powerful nucleophile when transferred to benzene.[3,8,13,14] Earlier, we used PEG to transfer potassium acetate to benzene for substituting benzyl chloride at room temperature (eq 1).[3]

$$RCl\ (\text{in } C_6H_6) + KOAc(s) \xrightarrow{\text{R-PEG}} ROAc + KCl \quad (1)$$

Applying these same conditions to reaction of 1 produced no reaction. However, upon raising the reaction temperature to the boiling point of benzene, reaction to produce the acetate did occur; half-life for disappearance of 1 is 3 h (Table I). Without the phase-transfer agent there is no reaction even after several hours. The product acetate was isolated and identified, and alkene was shown not to form (gas chromatography), so it is apparent that acetate is not acting as a base in this reaction.

In order to determine whether this acetate product was produced by direct substitution or by rapid attack on sulfonium ion, we have compared reaction rates under phase-transfer and hydrolytic conditions for 1 and *n*-octyl bromide; this latter compound was chosen to serve as a direct displacement model.[10] Table I includes rates in aqueous acetone and under phase-transfer conditions for *n*-octyl bromide and mustard chlorohydrin (1). Shifting reaction from water to the nonpolar organic phase by phase-transfer catalysis would be expected to favor a shift in mechanism from k_Δ to direct displacement. In the k_Δ process neutral reactants form an ion-pair-like transition state, so the process should be strongly disfavored by the shift from water to less highly ionizing benzene. On the other hand, the transition state for direct displacement by acetate produces a dispersal of charge and should be only slightly affected by solvent ionizing power.[15] Also, as noted, the anionic acetate reactant would be much more reactive in benzene. The effect of this shift in reaction conditions on a direct displacement process is illustrated by the hydrolysis to phase-transfer ratio of 3.0 for *n*-octyl bromide (Table I).

Table I. Solvolysis (50% v/v Acetone) and Phase-Transfer (C_6H_6/KO_2CCH_3) Rates for Reaction of Mustard Chlorohydrin (1) and *n*-Octyl Bromide (3)

compd	medium	T, °C	$10^5 k$, s^{-1}
3	50% acetone	74.8	1.14 ± 0.09
		84.7	2.43 ± 0.08
		80[a]	1.71
		25[a]	0.0119
	C_6H_6/KOAc	80	0.58 ± 0.03
1	50% acetone	25	55.9 ± 0.7
		45	276 ± 12
		80[a]	2950
	C_6H_6/KOAc	80	7 ± 2

[a] Calculated.

The effect on reaction of 1 of changing from hydrolytic to phase-transfer conditions is to produce a large decrease in rate (hydrolysis to phase-transfer rate ratio of 420). This retardation is consistent with the hydrolytic process being a k_Δ process. Next we must ask if there has been a shift to a direct displacement mechanism under phase-transfer conditions. That this shift may have occurred is indicated by the rate decrease for 1 upon changing from hydrolysis to phase transfer and also by the decrease in rate ratios for 1 relative to *n*-octyl bromide (Table I) from 1700 in aqueous acetone to 12 in benzene. However, the fact that the primary chloride 1 is more reactive than the primary bromide 3, despite bromide being a better leaving group, indicates that 1 is still reacting via a k_Δ process even under these unfavorable conditions. Again the power of neighboring sulfur participation is emphasized. Attempts to confirm this conclusion by use of the deuterium-labeled dinitrophenolate used in our earlier study[9] were foiled by the inertness of this derivative under these conditions.

It is also pertinent to ask if the direct displacement process for 1 is retarded relative to that for other primary halides; note that sulfur and carbon have similar electronegativities. The present data provide no information on this question, however, since the k_Δ process intervenes to give a reaction rate which is larger than that for *n*-octyl bromide. The following reaction does permit comment on this point.

Alkylation. The second phase-transfer reaction we have examined is alkylation of phenylacetonitrile by alkyl halides (eq 2). Regen has shown that this reaction pro-

$$RX + C_6H_5CH_2CN + 60\%\ KOH \xrightarrow{\text{PEG}} C_6H_5CHRCN + KCl \quad (2)$$

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ceeds rapidly at room temperature for alkyl bromides.[6] Since our previous reaction, acetate substitution, required 80 °C for reaction, this alkylation offers the possibility of a more facile process which may effectively compete with neighboring sulfur participation. Note that the nitrile acts as organic phase for this reaction; no additional organic solvent is added. We have used both R-PEG and PEG as phase-transfer agents.

Subjecting 1-bromobutane to the alkylation conditions gives complete disappearance (by gas chromatography) of reactant after 45 min. Interestingly, R-PEG and PEG are equally effective. Surprisingly, however, 1 proved to be unreactive under these conditions. The nitrile itself undergoes slow decomposition (as indicated by darkening and solid formation). After several hours this decomposition has proceeded extensively, yet reactant 1 remains unchanged (as indicated by gas chromatography).

One would expect the k_Δ process to be disfavored under these conditions, as it was in benzene (above). Unfortunately, however, it appears that alkylation by direct substitution is also sufficiently slow as to be uncompetitive with the decomposition pathway of phenylacetonitrile in the presence of concentrated base. Since direct displacement on 1 is much slower than that for *n*-butyl bromide, we can conclude that direct displacement on 1 is at least somewhat retarded; normal bromide/chloride rate ratios for direct displacement are rather small.[16]

Elimination. Primary alkyl halides are subject to E2 elimination under basic conditions.[17] Thus it could reasonably be expected that 1 would give elimination under phase-transfer conditions, where the k_Δ process is disfavored, even though elimination does not occur for either 1 or 2 at pH 10.[11]

PEG has been shown by Regen to be an effective catalyst for elimination in a benzene–60% aqueous KOH system (eq 3).[5] This observation is somewhat surprising in view of PEG partitioning strongly in favor of water relative to benzene in dilute solution,[3,4] but we have subsequently found that the concentrated base "drives" the PEG to the benzene layer. It is interesting to note Regen's

$$\mathrm{RCl\ (in\ C_6H_6)} + 60\%\ \mathrm{KOH} \xrightarrow{\mathrm{PEG}} \mathrm{alkene} + \mathrm{KCl} \quad (3)$$

observation that PEG apparently does not act in this case by transfer of hydroxide to benzene, but rather the PEG alkoxide itself acts as the base. This interpretation is based on the observation that the dimethyl ethers of PEG are not effective.[5]

Reaction of 1 under the conditions of eq 3 proceeded rapidly, with complete disappearance of reactant after 30 min. Reaction did not occur in the absence of phase-transfer agent. Again, PEG and R-PEG were equally effective. Product was isolated and determined to be the expected alkene; substitution did not occur. Since the sulfonium ion formed from the k_Δ pathway would be expected to give more substitution product even under these basic conditions, it is apparent that the k_Δ pathway is not involved, and one can conclude that the elimination pathway is dominant under these conditions.

Oxidation. As a final reaction we have examined phase-transfer-catalyzed oxidation of 3, with 5% aqueous sodium hypochlorite at room temperature. Reaction of 3 under these conditions proceeds with great vigor, and is apparently over within seconds. Upon mixing reagents there is an immediate evolution of heat and disappearance of 3 from our gas chromatographic trace. Gas chromatography indicates that a complex mixture of products is formed. From the proton NMR spectrum alkene (SC-H=CH_2), sulfoxide (SOCH), and sulfone (SO_2CH) peaks were identified. The alkene is expected since hypochlorite ion is also a strong base. In the absence of phase-transfer agent, reaction for several hours produced no detectable product.

Conclusions

In summary, phase-transfer-catalyzed elimination with potassium hydroxide and oxidation with hypochlorite are sufficiently facile to displace neighboring sulfur participation (k_Δ mechanism) as the dominant pathway for reaction of β-thioethyl chlorides. On the other hand, phase-transfer-catalyzed nucleophilic substitution by acetate is not sufficiently facile to be competitive. Similarly, alkylation by phenylacetonitrile is insufficiently reactive to give reaction. These results emphasize the power of the neighboring group process and indicate that the direct displacement process is somewhat retarded for these chlorides. Both PEG and its nonylphenyl ether are effective phase-transfer catalysts for the processes studied.

Experimental Section

Unless otherwise noted, reagents were purchased from Aldrich or Fisher. Nonylphenyl ether of PEG having thirteen ethylene oxide units (known as tergitol NP-13) and PEG (M_r 1900) were purchased from Union Carbide. Mustard chlorohydrin (1) was synthesized as described previously[18] and stored at −5 °C as a dilute solution in ether. Gas chromatographic analyses were performed on a Varian Model 4600 chromatograph with a 50-m Carbowax 20M capillary column. NMR analyses were performed on a 90-MHz Bruker spectrometer. Solvolysis kinetics were performed conductimetrically using conductivity cells[19] and a Hewlett-Packard data acquisition system described previously.[20]

Acetate Substitution. A benzene solution (10 mL, 20% w/v) of alkyl halide also containing 0.5 g of PEG or tergitol was added to 1.5 g of solid, dry potassium acetate and the resulting suspension heated to reflux. Samples were withdrawn by syringe periodically for GC analysis of alkyl halide disappearance and product acetate appearance. These concentrations were used to calculate the pseudo-first-order rate constants of Table I. It should be noted that the rates obtained by this procedure are a function of all the system parameters including stirring rate, volume ratios, and container geometry. These parameters were held constant to permit comparison for the different substrates.

The monoacetate of thiodiglycol was synthesized by adding 2-mercaptoethanol to vinyl acetate:[21] ^{1}H NMR ($CDCl_3$) 4.41 (t, 2 H, CH_2O_2C), 4.07 (s, 1 H, OH), 3.90 (t, 2 H, CH_2OH), 2.86 (m, 4 H, CH_2S), 2.14 (s, 3 H, CH_3) ppm.

Alkylation. Tergitol or PEG (0.5 g) was added to 10 mL of a 20% (v/v) solution of alkyl halide in phenylacetonitrile, and then this solution was added to 10 mL of 60% (w/w) aqueous potassium hydroxide. The resulting two-phase system was stirred magnetically at room temperature. Samples were withdrawn by syringe for GC analysis of alkyl halide disappearance.

Elimination. This reaction was performed identically to the alkylation reaction except that the phenylacetonitrile was replaced with benzene. The alkene was identified by GC comparison with an authentic sample prepared by this same process. The alkene was removed by warming the system to 60 °C and collected in a liquid nitrogen trap: ^{1}H NMR ($CDCl_3$) 6.39 (q, 1 H, CH), 5.01

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(q, 2 H, CH_2), 4.11 (s, 1 H, OH), 3.92 (t, 2 H, CH_2OH), 2.90 (t, 2 H, CH_2S) ppm.

Oxidation. This reaction was performed identically to the elimination except that the 60% hydroxide solution was replaced with 5% sodium hypochlorite.

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Registry No. 1, 693-30-1; PEG, 25322-68-3; octyl bromide, 111-83-1; 2-(methylthio)ethyl chloride, 542-81-4; tergitol NP-13, 9016-45-9; potassium acetate, 127-08-2; thiodiglycol monoacetate, 2020-50-0; [(2-hydroxyethyl)thio]ethene, 3090-56-0; phenylacetonitrile, 140-29-4; 2-mercaptoethanol, 60-24-2; vinyl acetate, 108-05-4.

Stereoselective Synthesis of Trisporic Acids A and B, Their Methyl Esters, and Trisporols A and B, Hormones and Prohormones of Mucoraceous Fungi[1]

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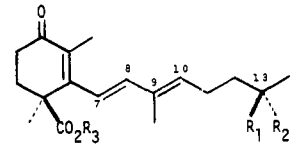
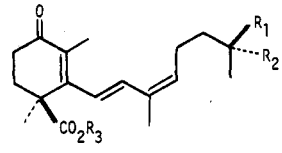
Syntheses of (9*E*)- and (9*Z*)-trisporic acids A (**1** and **4**) and B (**2** and **5**) and the corresponding methyl esters (**7**, **10**, **8**, and **11**, respectively) were accomplished via the Wittig reaction of lactol **52** with an appropriate phosphorane. The lactol was prepared by means of a Robinson annulation of α-methyltetronic acid with ethyl vinyl ketone to give **36**, followed by allylic bromination and hydrolysis. Methyl O^4,4-dihydrotrisporate B (**17**) was also synthesized by this route, confirming the structural and stereochemical assignment previously made to this prohormone of *Blakeslea trispora*. Trisporols A (**92**) and B (**13**) were obtained by a variant of this pathway, in which γ alkylation of the dianion **62** with the appropriate *Z* allylic bromide was followed by Robinson annulation with ethyl vinyl ketone. Bioassay of the synthesized hormones and prohormones with mating strains of *Mucor mucedo* showed that trisporic acids of the A series are inactive, whereas the B acids and their esters are active with both strains. Trisporols A and B and methyl O^4,4-dihydrotrisporate are strain-specific in their ability to induce zygophore formation.

Heterothallic fungi of the order Mucorales propagate through the union of sexually differentiated mating types.[2] The development of oppositely sexed ("plus" and "minus") mating strains as well as the mating process which leads to zygospore formation is mediated by a family of C_{18} isoprenoid substances consisting inter alia of (9*E*)-trisporic acids A (**1**), B (**2**), and C (**3**), their 9*Z* isomers **4**, **5**, and **6**, and the corresponding methyl esters **7**–**12**.[3] Extensive biological studies by van den Ende,[4] Sutter,[5] and Gooday[6] lend credence to the view that these carotenoid-derived substances both regulate the first stages of sexual development and stimulate the production of zygophores (sex cells) in organisms such as *Phycomyces blakesleeanus*, *Mucor mucedo*, and *Blakeslea trispora*. Further studies have demonstrated that certain prohormones or "pheromones", which are specific to each mating strain,[7] are transmitted to the sexual partner and converted to trisporic acids at the stage of zygophore induction.[8] These prohormones include trisporols B (**13**) and C (**14**),[9] trisporins B (**15**) and C (**16**),[10] and a substance tentatively



1, $R_1=R_2=R_3=H$
2, $R_1,R_2=O$, $R_3=H$
3, $R_1=OH$, $R_2=R_3=H$
7, $R_1=R_2=H$, $R_3=CH_3$
8, $R_1=R_2=O$, $R_3=CH_3$
9, $R_1=OH$, $R_2=H$, $R_3=CH_3$
54 $R_1,R_2=OCH_2CH_2O$, $R_3=H$
56 $R_1,R_2=OCH_2CH_2O$, $R_3=CH_3$



4, $R_1=R_2=R_3=H$
5, $R_1,R_2=O$, $R_3=H$
6, $R_1=R_3=H$, $R_2=OH$
10, $R_1=R_2=H$, $R_3=CH_3$
11, $R_1,R_2=O$, $R_3=CH_3$
12, $R_1=H,R_2=OH$, $R_3=CH_3$
55, $R_1,R_2=OCH_2CH_2O$, $R_3=H$
57, $R_1,R_2=OCH_2CH_2O$, $R_3=CH_3$

assigned structure **17**.[9,10] As an illustration of this cooperative behavior, it was shown that trisporins and trisporols, which are produced only by minus cultures of *B. trispora*, were converted by the oppositely sexed plus strain into **5** and **6**, whereas **17** from the plus type was trans-

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