1380 (m), 1272 (s), 1175 (s), 1088 (s), 855 cm^{-1} (m); NMR (CCl_4) δ 1.30 (d, J = 6 Hz, 3 H), 1.78 (m, 6 H), 2.22 (s, 9 H), 5.20 (d, J = 10 Hz, 1 H, vinyl), 5.50–6.05 (m, 1 H), 6.70 (s, 2 H, aromatic).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 77.99; H, 9.00. Found: C, 77.86; H, 8.93.

Reaction of Mesitoate Ester 7 with Carbonyl Compounds. The ester (0.05 mol) and the carbonyl compound (0.05 mol) were allowed to stir in 50 ml of dry THF with an excess (0.5 mol) of lithium metal. When all of the ester was consumed (TLC), the reaction was quenched and a standard aqueous workup employed to isolate the carbinol product(s). Pure samples were prepared by preparative GLC.

Reaction with Acetone. Compound **8**: 49% yield; ir (neat) 3520 (s), 3020 (w), 2960 (s), 1610 (w), 980 cm^{-1} (s); NMR (CCl_4) δ 1.00 (s, 6 H), 1.07 (s, 6 H), 1.75 (d, J = 5 Hz, 3 H), 4.60 (s, 1 H, –OH), 5.58 (m, 2 H, vinyl).

Anal. Calcd for $C_9H_{18}O$: C, 75.98; H, 12.76. Found: C, 75.83; H, 12.82.

Reaction with Cyclohexanone. Compound **9**: 35% yield; ir (neat) 3500 (s), 3040 (s), 2900 (s), 1630 (m), 1450 (s), 1380 (s), 1320 (m), 1270 (s), 1138 (s), 982 (s), 852 cm^{-1} (m); NMR (CCl_4) δ 1.00 (s, 6 H), 1.47 (s, 10 H), 1.76 (d, J = 5 Hz, 3 H), 2.33 (s, 1 H, –OH), 5.58 (m, 2 H, vinyl).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.04; H, 12.17. Found: C, 78.97; H, 12.08.

Reaction with 2,2-Dimethylpropanal. Compounds **10** and **11**, 83% yield overall, 1:2 ratio, respectively.

Compound **10**: ir (neat) 3500 (s), 2900 (s), 2870 (s), 1670 (s), 1480 (s), 1445 (s), 1360 (s), 1080 (s), 980 (s), 840 cm^{-1} (s); NMR (CCl_4) δ 0.90 (s, 9 H), 1.00 (d, J = 6 Hz, 3 H), 1.40 (s, 1 H, –OH), 1.67 (m, 6 H), 2.20 (m, 1 H), 3.10 (d, J = 3 Hz, 1 H), 5.20 (d, J = 9 Hz, 1 H).

Anal. Calcd for $C_{11}H_{22}O$: C, 77.56; H, 13.03. Found: C, 77.42; H, 12.71.

Compound **11**: ir (neat) 3510 (s), 3045 (m), 2900 (s), 1665 (w), 1460 (s), 1265 (m), 1140 (s), 980 cm^{-1} (s); NMR (CCl_4) δ 0.95 (s, 9 H), 1.10 (s, 6 H), 1.68 (d, J = 4.5 Hz, 3 H), 2.30 (s, 1 H), 3.00 (s, 1 H, –OH), 5.42 (m, 2 H, vinyl).

Anal. Calcd for $C_{11}H_{22}O$: C, 77.56; H, 13.03. Found: C, 77.76; H, 12.82.

3,3,5,5-Tetramethylhexen-4-ol (13). 2,2-Dimethylpropanal (0.05 mol) and 2-methyl-4-bromo-2-butene (**12**, 0.05 mol) were treated in dry THF with an excess of magnesium[11] or lithium.[12] Following a standard aqueous workup, the carbinol product **13** was distilled (109–110 °C, 30 Torr). Yield in both cases was approximately 82%; ir (neat) 3500 (s), 3090 (w), 2970 (s), 2880 (s), 1632 (w), 1480 (m), 1365 (m), 1050 (s), 1005 (s), 987 (s), 905 cm^{-1} (s); NMR (CCl_4) δ 1.00 (s, 9 H), 1.18 (s, 6 H), 2.00 (s, 1 H), 3.08 (s, 1 H, –OH), 4.78–5.10 (m 2 H) 6.02 (d of d, J_a = 19, J_b = 10 Hz, 1 H).

Anal. Calcd for $C_{10}H_{20}O$: C, 76.84; H, 12.91. Found: C, 76.57; H, 12.83.

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Registry No.—**1d**, 58602-59-8; **3**, 4325-82-0; **7**, 58602-60-1; **8**, 58602-61-2; **9**, 58602-62-3; **10**, 58602-63-4; **11**, 58602-64-5; **12**, 870-63-3; **13**, 58602-65-6; mesityl oxide, 141-79-7; mesitoyl chloride, 938-18-1.

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Tetrabenzylethylene. An Unusually Sterically Hindered Olefin

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Current interest in the properties of sterically hindered olefins[1] prompts us to report our results with tetrabenzylethylene (**1**). In the course of an attempt to prepare a bromohydroperoxide from **1**, we found that **1** was rather inert to the addition of bromine in carbon tetrachloride.[2] Similarly, **1** was inert to potassium permanganate solution[2] over a 25-min period as well as being inert to 2,4-dinitrobenzenesulfonyl chloride[2] and mercuric acetate.[3] The well-known inertness of tetraphenylethylene[4] is usually attributed solely to resonance stabilization of the olefinic bond. However, in view of the inert behavior of **1**, the steric effect of four phenyl groups in close proximity to the olefinic bond may be sufficient for inert behavior.

In order to assess the steric effects in **1**, the rate of bromination in acetic acid at 24.0 °C was measured by an iodometric method.[5] A second-order rate coefficient of $8.68 \pm 0.29 \times 10^{-4}$ M^{-1} s^{-1} was obtained with the reaction mixture under a nitrogen blanket and protected from light. A considerable amount of rate data obtained by Robertson and co-workers for bromination of olefins under these conditions has been compiled.[6] Most of these rates can be correlated with the Taft polar effect equation (eq 1)

$$\log k = \rho^* \Sigma\sigma^* + a_0 \qquad (1)$$

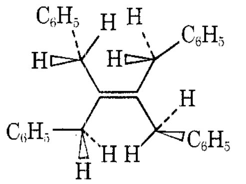
where $\rho^* = -2.58 \pm 0.099$, and $a_0 = 4.85 \pm 0.25$ with r (correlation coefficient) = 0.992. With these values for eq 1, the calculated bromination rate of **1** is 4.28×10^2 M^{-1} s^{-1} at 24 °C. Thus, steric effects in **1** causes a reduction in rate of about 5×10^5-fold ($= 4.28 \times 10^2 / 8.68 \times 10^{-4}$).

Dubois and Mouvier[7] reported the rates of bromination of olefins in methanol at 25 °C with 0.2 M sodium bromide, where steric effects in a few olefins were significant. These data are best correlated with the Taft polar–steric effect equation (eq 2)

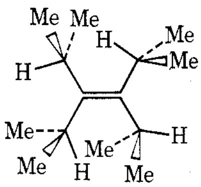
$$\log k = \rho^* \Sigma\sigma^* + \delta \Sigma E_s + a_0 \qquad (2)$$

where $\rho^* = -5.30$, $\delta = 0.913$, and $a_0 = 5.64$ with $r = 0.999$.[8] To compare our data in acetic acid at 24 °C to the data of Dubois and co-workers in methanol at 25 °C, we have calculated the relative rate of bromination of **1** in methanol (1.52×10^3 M^{-1} s^{-1}) to acetic acid (4.28×10^2 M^{-1} s^{-1}) where polar effects alone correlate the data.[8] With this factor ($1.52 \times 10^3 / 4.28 \times 10^2 = 3.55$), our experimental rate coefficient in acetic acid becomes 3.08×10^3 M^{-1} s^{-1} ($= 3.55 \times 8.68 \times 10^{-4}$ M^{-1} s^{-1}) in methanol. Now a calculated value of the rate of bromination of **1**, with eq 2 and the parameters from the data of Dubois and Mouvier,[7] is 4.91×10^{-1} M^{-1} s^{-1}. The experimental rate for **1** is then about 160-fold slower than predicted ($4.91 \times 10^{-1} / 3.08 \times 10^{-3} = 160$). Inclusion of **1** into a correlation of the data of Dubois and Mouvier[7] by eq 2 gives a larger δ value; $\rho^* = -6.55$, $\delta = 1.41$, and $a_a = 5.70$ with $r = 0.990$. This may be a more reliable correlation, since it extends the range of E_S values of the olefins by including **1**.[9]

An examination of space-filling molecular models suggests that **1a** is a low-energy conformation of tetrabenzylethylene. Previously, ^1H NMR studies of tetraisopropylethylene indicated a "cogwheel" effect with a high barrier to rotation, which involved conformation **2**.[1] Two distinct tertiary protons were observed due to their disposition about the olefinic bond. Since conformation **1a** suggests unique protons, the ^1H NMR

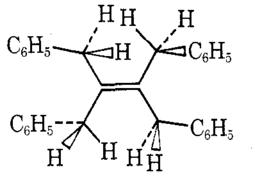


1a



2

spectrum of 1 was measured from approximately 30 to −30 °C in carbon tetrachloride solution. Over this temperature range, the benzyl protons of 1 remained as a singlet. This suggests that the "cogwheel" effect is inoperative with 1. Instead, it seems most reasonable that a rapid equilibrium may occur between conformations **1a** and **1b** such that unique protons are not detected over this temperature range.



1b

In summary, the bromination rate of 1 dramatically demonstrates the importance of steric effects in addition reactions of olefins.[9] Without a consideration of steric effects, the experimental rate is slower by a factor of about 5×10^5-fold. However, an excellent correlation[11] by eq 2 results when steric effects are included. It is apparent that the mere proximity of phenyl groups to the olefin bond is sufficient to cause slow rates of addition reactions. Lastly, ^{1}H NMR data suggest that a "cogwheel" effect is not operative with 1.

Experimental Section[12]

2,3-Dibenzyl-1,4-diphenyl-2.3-butanediol (3). A mixture of 9.95 g (47.3) mmol) of dibenzyl ketone (MCB, recrystallized from cyclohexane), 0.540 g (20.0 mg-atoms) of aluminum foil (Reynolds Wrap, sanded prior to use), 0.10 g (0.368 mmol) of mercuric chloride, and 150 ml of benzene (reagent grade, distilled from calcium hydride) was stirred and heated at 60–70 °C for 24 h under a nitrogen atmosphere. The reaction mixture was then cooled in an ice bath while 100 ml of 5% hydrochloric acid was added over a 2.0-h period. The organic layer was separated and the aqueous phase was extracted with carbon tetrachloride. The combined organic phases were washed with water, dried over anhydrous potassium carbonate, and concentrated on a rotary evaporator to give 9.34 g of a viscous yellow oil. NMR analysis of this oil, relative to a measured amount of methylene chloride, indicated a 48% yield of pinacol **3**. Chromatography of the oil (9.3 g) on silica gel (70 g) with 10% benzene–90% *n*-hexane eluent gave 4.23 g (42.3% yield) of **3**: mp 118–120 °C (lit.[13] mp 120 °C); ir 3560, 3090, 3060, 3030, and 2940 cm^{-1}; NMR OH (1.77, s, 1.94), $C_6H_5CH_2$ [2.92, AB (J = 14 Hz), 8.0], and C_6H_5 (7.08, s, 19.6).

Tetrabenzylethylene (1). A solution of 9.09 g (21.5 mmol) of pinacol **3**, 15.0 ml (13.5 g, 90.9 mmol) of ethyl orthoformate (dried over calcium sulfate and distilled at 146 °C), and 0.10 g (0.82 mmol) of benzoic acid was stirred and heated at 148–155 °C (internal temperature) for 9.0 h under a nitrogen atmosphere. During this period 2.0 ml (ca. 80% of theory) of ethanol was distilled from the reaction solution. The excess ethyl orthoformate was distilled and the residual oil was heated with 0.20 g (1.6 mmol) of benzoic acid for 16 h. The reaction mixture was then dissolved in 25 ml of carbon tetrachloride and this solution was washed with 0.2 M potassium carbonate and with water. The organic solution was dried over calcium sulfate and rotary evaporated to 8.31 g of a yellow, oily solid. Recrystallization from *n*-hexane gave 6.60 g (82.8% yield) of white needles of **1**: mp 119.7–120.7 °C (lit.[14] mp 119.5–120.5 °C); ir 3080, 3060, 3025, 2960, 2920, and 2850 cm^{-1}; NMR CH_2 (3.47, s, 8.00), C_6H_5 (7.10, s, 20.0); mass spectrum, P *m/e* 388 (12), P − $C_6H_5CH_2$ 297 (9.0), P − ($C_6H_5CH_2$, C_6H_5, and H) 219 (12), P − [2($C_6H_5CH_2$) and H] 205 (13), P − [2($C_6H_5CH_2$), H, and C] 193 (3.9), and $C_7H_7^+$ 91 (100).

Kinetics of Bromination. An acetic acid solution of 1 and bromine (each 7.63×10^{-3} M) were placed in an aluminum foil wrapped vessel under a nitrogen atmosphere, which was thermostated at 24.0 °C. Aliquots were periodically withdrawn and titrated by an iodometric procedure.[5] The second-order rate coefficients were obtained by a least-squares fit.

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Registry No.—**1**, 19754-02-0; **3**, 33574-71-9; dibenzyl ketone, 102-04-5.

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Remote Substituent Effects on Carbon-13 Shieldings in Some Bicyclo[2.2.2]octyl Systems

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Fluorine-19 chemical shifts of certain dibenzobicyclo[2.2.2]octyl derivatives, e.g., adducts of 10-substituted 9-fluoroanthracenes with maleic anhydride (I) and dimethyl acetylenedicarboxylate (II), have been studied in anticipation that these ^{19}F substituent chemical shifts (^{19}F SCS) might approximate to the field component of the overall ^{19}F SCS in aromatic fluorides where direct partitioning of components is impossible.[2] Although structural deformations in some bicyclic tertiary fluorides are apparently to blame for worrying fluctuations in chemical shift, Anderson and Stock reasoned