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the nitrone spin trap PBN.[2a] For example, *tert*-butylethylene gives a radical yield of 0.1% using the BHT method; PBN gives a radical yield of 0.004% with this olefin, confirming our suggestion[2a] that PBN traps radicals with about 1% efficiency in these ozone systems.[2b]

This work demonstrates the usefulness of BHT as a "spin trap". Carbon-centered radicals can be converted to peroxyl radicals in the presence of oxygen, and BHT traps these radicals with high efficiency. The use of BHT in place of a nitrone spin trap clearly conveys some advantages: BHT yields a stable, diamagnetic species that can be quantified by normal chromatographic methods, rather than by ESR. While the identification of the radical that is trapped by BHT using GC/MS is not trivial, our data do show that this identification can be made (at least for simple R groups) using GC/MS in collaboration with NMR.

Acknowledgment. This work was supported in part by grants from the National Science Foundation, the National Institutes of Health (HL-16029), and a Contract from the National Foundation for Cancer Research.

Supplementary Material Available: Figure 1, IR spectra, Figure 2, ^1H NMR spectra, and Figure 3, ^{13}C NMR spectra of compounds 1 and **2a** (3 pages). Ordering information is given on any current masthead page.

Triphenylborane Methanolysis and Equilibrium Association between Triphenylborane or Diphenylborinate Esters and Alcohols

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Treatment of triphenylborane (TPB) with simple alcohols (ROH) results in varying extents of $TPB(ROH)_n$ complex formation. Equilibrium formation constants strongly depend on steric bulk of the alcohol and range from about 300 for methanol where $n = 3$ to zero for *tert*-butyl alcohol. Steric effects are also important in the ester exchange reaction: $R^1OH + Ph_2BOR \rightleftharpoons ROH + Ph_2BOR^1$. Alcoholysis of TPB to give Ph_2BOR + benzene is catalyzed by acids, bases, and certain metals and is inhibited by excess alcohol. The rates of methanolysis of TPB were measured by ^1H NMR and IR at room temperature for different TPB/methanol ratios and the kinetics modeled by computer. The rate is first order in TPB and zero order in methanol.

Two aspects of triarylborane chemistry have received considerable study: association of such boranes with a variety of bases and protonolysis of the B–C bond.[1,2] Bases which undergo complexation with triarylboranes include hydroxide, alkoxide, cyanide, amines, and nitriles.[3] Steric effects strongly affect complex formation strengths as first delineated by brown and co-workers in their studies of steric strain in trialkylborane/amine complexes.[4] Little has been reported about equilibrium association between triarylboranes and alcohols, perhaps owing to the weakness of such interactions and to the fact that simple alcohols in nonpolar solvents exist largely as mixtures of dimers, trimers, tetramers, ...*n*-mers, thus adding analytical complexisy.[5] The B–C bond of triaryl- or trialkylboranes can undergo protonolysis but generally requires catalysis by acids or bases. For example, pure trialkylboranes are remarkably stable toward hydrolysis.[6] Likewise, $PhB(OH)_2$ underwent only 0.07% methanolysis when heated at reflux for 6 days in methanol.[7] This paper summarizes a study of methanolysis of triphenylborane (TPB) and includes a kinetic model which takes into consideration equilibria for MeOH self-association and complexation between TPB and MeOH. It is concluded that the rate of $Ph_2B(OMe)$ formation is first order in TPB and zero order in MeOH concentrations, when catalyzed by carboxylic acids or certain active metals.

Table I. ^{11}B NMR Chemical Shifts for TPB and Its Reaction Products and Equilibrium Association Complexes with Methanol in Freon-11 at 25 °C

compd	^{11}B chem shift[a]	ref
TPB	+68.0	
$Ph_2B(MeO)$	+45.7	
$TPB(MeOH)_n$	+39.0	
$PhB(OMe)_2$	+29.0	
$Ph_2B(OEt)$	+45.1	8
$PhB(OMe)_2$	+28.6	9
$PhB(OEt)_2$	+28.6	10
$B(OMe)_3$	+18.2	11
$B(OEt)_3$	+17.6	12

[a] Chemical shifts are referenced to $BF_3 \cdot Et_2O$ with positive values to higher frequencies.

Reversible Complex Formation

TPB complexes reversibly with alcohols, the stabilities of the $TPB(ROH)_n$ complexes varying inversely with increasing steric size of the alcohol (eq 1). Evidence for

$$TPB + n\text{-}ROH \rightleftharpoons TPB(ROH)_n \qquad (1)$$

formation of $TPB(ROH)_n$ complexes was obtained from IR, ^{11}B, ^{13}C, and ^1H NMR, and UV spectra. A CCl_4 solution containing 0.5 M amounts of TPB and methanol

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0022-3263/85/1950-0189$01.50/0

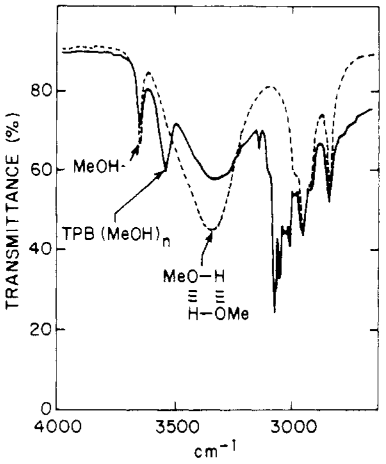
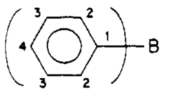


Figure 1. IR spectra of CCl_4 solutions containing 0.48 M MeOH (- - -) and 0.50 M MeOH plus 0.30 M TPB (—).

(MeOH), for example, gives a broad band centered at 3320 cm^{-1} and a weak sharp band at 3650 cm^{-1}, assignable to $(MeOH)_n$ hydrogen-bonded species and to free MeOH, respectively. A medium intensity band at 3550 cm^{-1} is assigned to $TPB(MeOH)_n$ complexes (Figure 1). Measurements using ^{11}B NMR also provided qualitative evidence for the presence of free and complexed TPB. ^{11}B chemical shifts (ppm) of TPB, $PhB(OMe)_2$, $Ph_2B(OMe)$ and a solution containing TPB and $TPB(MeOH)_n$ are given in Table I. The chemical shift of +39.0 ppm for $TPB(MeOH)_n$ complexes was recorded for a solution containing 0.32 M TPB and 1.0 M MeOH. From the computer model described below (see Experimental Section), the ratio of $TPB(MeOH)_n/TPB$ was calculated to be about 70/30.

The dependence of ^{13}C NMR chemical shifts on MeOH/TPB ratio was determined for a series of solutions in CCl_4 at 25 °C. Each solution contained 0.2 M TPB and MeOH varying from 0 to 1.0 M. All ^{13}C resonances shifted from high to low field, including that of MeOH, with increasing MeOH concentration. The resonances assigned to C-2 showed the largest sensitivity and varied from 138.36 (no MeOH) to 135.77 (1.05 M MeOH) to 134.96 for 0.2 M TPB in neat MeOH. Based on the computer model, the ratio of $TPB(MeOH)_n/TPB$ in the neat MeOH solution should be >99/1 (see Experimental Section). The observed changes in ^{13}C chemical shifts support the claim of equilibrium association between the TPB and MeOH. ^1H NMR measurements using similar solutions of TPB and MeOH showed that the OH proton in $TPB(MeOH)_n$ complexes is deshielded relative to that of the free alcohol, and its ^1H NMR chemical shift is the weighted average of all contributors. In the case of 1 M MeOH in CCl_4, the OH shift varied from 4.135 to 4.563 ppm for TPB concentrations from 0.1 to 0.5 M.



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UV spectroscopy provided the most quantitative measure of the magnitude of association constants for TPB and different alcohols, including the number of moles of alcohol complexed in the predominant complex. All solutions contained 3.5 × 10^{-3} M TPB in CCl_4 and 0 to 5 M MeOH, EtOH, or *i*-PrOH. The 287-nm absorption band of uncomplexed TPB, assigned by Leffler and Ramsey to an intramolecular charge-transfer transition, was used as a measure of the amount of free TPB present.[13] As shown by Leffler, the 287-nm band is absent when TPB is dissolved in neat spectrograde acetonitrile, attributed to formation of a TPB/acetonitrile complex. The 287-nm band is also absent for a 3.5 × 10^{-3} M solution of TPB in neat MeOH. In Figure 2 is shown a plot of log $TPB(ROH)_n/TPB$ vs. log ROH_{free}. Concentrations of monomeric alcohols (ROH_{free}) as a function of total alcohol in CCl_4 were determined by using the equilibrium self-association constants for dimer, trimer, and tetramer reported by Saunders (Table II).[5] Figure 2 does not contain data for *t*-BuOH because no complex formation was observed by UV spectroscopy. Likewise, IR and ^1H NMR measurements gave no indication of complexation of *t*-BuOH with TPB, indicative of a very large steric effect in the complexation of TPB with alcohols. The plots in Figure 2 were used to calculate K_{equil} constants and values of n (eq 1). The decrease in K_{equil} in the series MeOH > EtOH > *i*-PrOH is, again, a reflection of steric effects. The values for n were all close to 3 and may indicate that TPB takes the place of one of the tetrameric alcohols. Alternatively, TPB may actually exist as a mixture of 1/1, 1/2, and 1/3 complexes. It was found necessary to take into account association between TPB and MeOH in order to achieve good matching of computer-generated and experimentally determined rate plots.

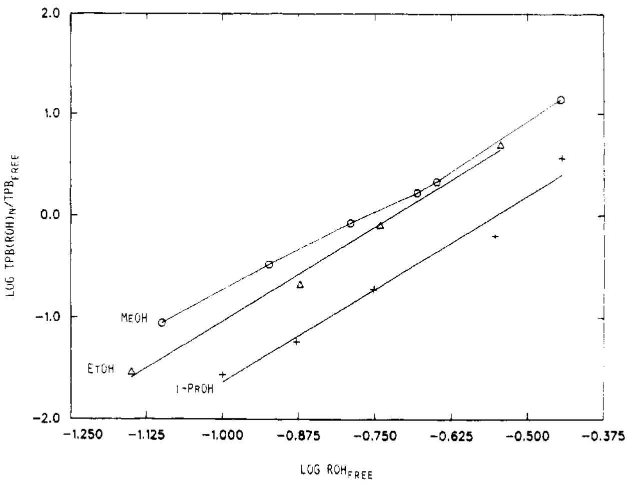

Figure 2. log $TPB(ROH)_n/TPB_{free}$ as a function of log ROH_{free} for MeOH (○), EtOH (△), and for *i*-PrOH (+).

Table II. Equilibrium Constants for Alcohol Self-Association and $TPB(ROH)_n$ Formation

	$(ROH)_{2-4}$			TPB + nROH $\rightleftharpoons^c$ $TPB(ROH)_n$	
ROH	$K_2{}^a$	$K_3{}^a$	$K_4{}^a$	K_{equil}	n
MeOH	0.6	2.8	28	316	3.3
EtOH	0.7	5.2	45	158	3.3
i-PrOH	0.7[b]	5.4[b]	47[b]	32	3.3
t-BuOH	0.7	5.6	50	0	

[a] K_2, K_3, and K_4 are alcohol equilibrium self-association constants for dimer, trimer, and tetramer formation reported by Saunders and Hyne.[5] [b] Values interpolated between data for EtOH and *t*-BuOH. [c] K_{equil}.

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(10) Phillips, W. D.; Miller, H. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1959**, *81*, 4496.
(11) Bogdanov, V. S.; et al. *J. Magn. Reson.* **1971**, *5*, 145.
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Table III. ^{1}H NMR Chemical Shifts for CCl_4 Solutions of 0.2 M $Ph_2B(O$-t-Bu) with 0.2 M MeOH, EtOH, i-PrOH, and t-BuOH

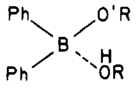
ROH, M	$(CH_3)_3C$ chem shift, ppm
t-BuOH[a]	1.203 1.351
MeOH	1.186
EtOH	1.186
i-PrOH	1.185
t-BuOH	1.185 (1)[a] + 1.351 (1)[c]
t-BuOH[b]	1.184 (0.08)[c] + 1.351 (1)[c]

[a] No $Ph_2B(O$-t-Bu) present. [b] t-BuOH = 0.05 M. [c] Values in parentheses are approximate integrals.

A series of equilibrium reactions was studied by using ^{1}H NMR which involved ester exchange between free ROH and the $Ph_2B(OR)$ alcoholysis product (eq 2). A stock

$$R^1OH + Ph_2B(OR) \rightleftarrows ROH + Ph_2B(OR^1) \quad (2)$$

solution containing 0.2 M $Ph_2B(O$-t-Bu) in CCl_4 was prepared and run by itself and with added 0.2 M concentrations of alcohols. The signal at 1.185 was assigned to the methyl group of free t-BuOH in the presence of $Ph_2B(OR)$ and was confirmed by spiking $Ph_2B(O$-t-Bu) with a small amount of t-BuOH. The results in Table III show that $Ph_2B(O$-t-Bu) reacts rapidly with MeOH, EtOH, and i-PrOH to give nearly completely the respective ester exchange products, $Ph_2B(OMe)$, etc., plus free t-BuOH. The exchange of t-BuOH with $Ph_2B(O$-t-Bu), on the other hand, does not occur rapidly enough on the NMR time scale to average methyl resonances. Evidently, there is sufficient space in the presumed ester exchange intermediate 2 to accommodate any combination of RO and R′O



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groups, when R and R′ are Me through t-Bu, except for the one case where both R and R′ are t-Bu.

Irreversible Methanolysis of TPB

In dry air-free solutions of TPB and alcohols, the major alcoholysis product is $Ph_2B(OR)$. Further reaction to form $PhB(OR)_2$ occurs only extremely slowly. For example, the product mixture from a toluene solution containing 0.34 M TPB and 0.36 M i-PrOH, analyzed by HPLC after 1 week, contained 8.7% $Ph_2B(O$-i-Pr) (8.5% theoretical) and 0% detected $PhB(O$-i-$Pr)_2$. That benzene is formed stoichiometrically with $Ph_2B(OR)$ formation was determined by ^{1}H NMR and IR. Whereas TPB, purified by repeated recrystallization from acetonitrile, reacts with stoichiometric amounts of alcohols very slowly, with half-lives of several days, reaction rates become even longer in the presence of greater than stoichiometric amounts of alcohols. Alcoholysis rates can be accelerated by catalytic amounts of acids, bases, moisture, and even by certain metals to a small extent. A convenient method of determining the effect of TPB and MeOH concentrations on methanolysis rate in CCl_4 solution was to measure intensities of the B–O–C IR stretching frequency at 1325 cm^{-1} in the $Ph_2B(OMe)$ product with time for a series of solutions containing different $[TPB]_0$ and $[MeOH]_0$ concentrations. The data shown in Figure 3 were obtained by leaving a 0.1-mm NaCl IR cell filled with the respective solutions for the duration of the rate measurements. The duraction of each measurement, about 2 min, was shown to be sufficiently brief to prevent thermal rate enhancement. The plots show qualitatively that the alcoholysis rates are proportional to $[TPB]_0$ but exhibit an apparent inverse dependence on $[MeOH]_0$ concentration. The rate inhibitory effect will be addressed below in the discussion of the computer modeling of the kinetics. Control experiments showed that TPB in a given solution underwent insignificant amounts of methanolysis when not exposed to the IR cell.

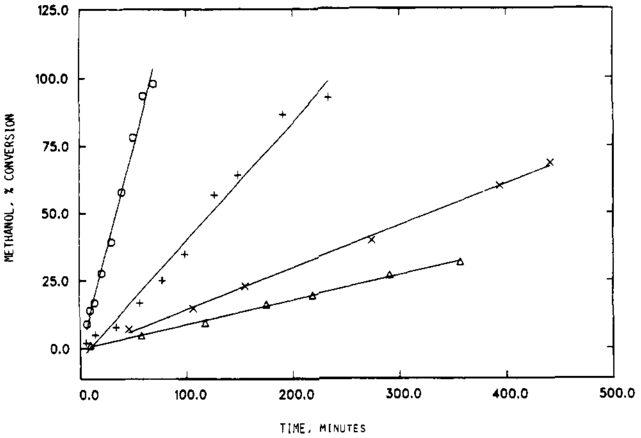

Figure 3. Methanol conversion as a function of TPB_0 and $MeOH_0$ concentration ratios, catalyzed by IR cell metal spacer and measured by IR. $TPB_0/MeOH_0$, M/M = 0.4/0.1 (○), 0.21/0.1 (+), 0.2/0.2 (×), and 0.4/0.4 (△).

A series of experiments was run to determine the extent to which metals, present in the 0.1-mm IR cell spacer, might act as catalysts for the reaction. The experiments showed that Cu and Zn exhibited small, but significant, catalytic activity, giving 3% to 4% conversion of methanol per hour (Experimental Section). The possibility that such catalysis might involve organometallic intermediates derived from CCl_4 solvent was excluded by repeating the experiments in toluene solvent. Very similar catalytic effects of Cu and Zn were again obtained. A series of experiments was also run using pure metal oxides in place of the metal (Experimental Section). The low catalytic activity from the metal oxides make it unlikely that catalysis by the metal IR cell spacer was primarily due to the presence of metal oxides. The possibility of radical chain catalysis, initiated by metals, was examined since the stability of the TPB radical anion is well known.[3,14]

An experiment was carried out in the presence of Luminol (2,4,6-trimethylphenol) to look for suppression of reaction rate. Two 0.5-cm^3 solutions were prepared, each containing 0.2 M TPB and 0.2 M MeOH in CCl_4 and 5 cm of coils of 0.25-mm diameter Zn wires. To one of the solutions was also added 0.04 M Luminol. After 18 h, the solution containing Luminol had undergone 50% methanolysis, compared with 60% conversion in the control solution. Such minimal rate retardation does not point to a radical chain mechanism. Similar experiments using $(CH_3)_3CC(CH_3)_2OH$ gave no evidence for acetone formation as would be expected for a radical reaction.[15,16] An ESR experiment was carried out by using 0.2 M TPB and 0.2 M MeOH in CCl_4 solution with a 5-cm coil of Zn wire and 0.02 M PhCH=N(O)-t-Bu as a radical trap. No signals assignable to spin adducts were detected. It is most likely that catalysis resulting from the IR cell spacer was due to the combined effects of metals and acidic and basic impurities.

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(15) $(CH_3)_3CC(CH_3)_2OH$ was used as a probe for radical reaction by Kochi, Nugent, and Bertini.[16]

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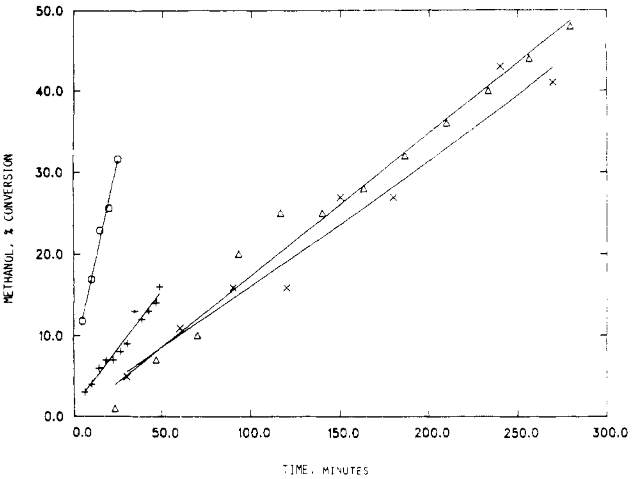

Figure 4. Methanol conversion as a function of TPB_0 and $MeOH_0$ concentration ratios, catalyzxed by 0.02 M CF_3CO_2H and measured by ^1H NMR. $TPB_0/MeOH_0$, M/M = 0.4/0.1 (○), 0.2/0.1 (+), 0.2/0.2 (×), and 0.4/0.4 (△).

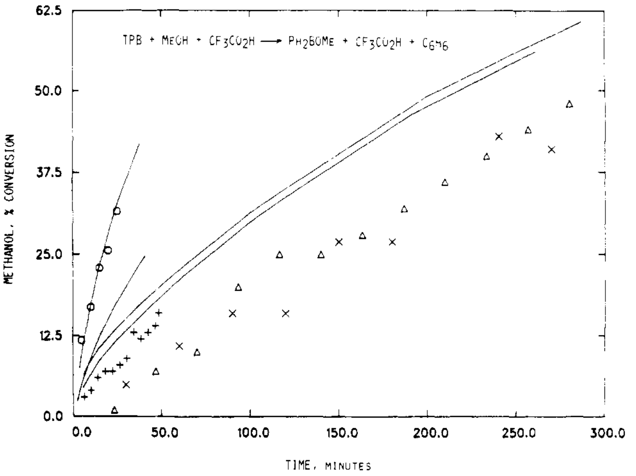

Figure 5. Comparison of methanol conversion rates determined by ^1H NMR (points) and by computer simulation (—). $TPB_0/MeOH_0$, M/M = 0.4/0.1 (○), 0.2/0.1 (+), 0.2/0.2 (×), 0.4/0.4 (△).

Table IV. Relative Rate of Methanolysis of TPB, Catalyzed by Protonic Acids, as a Function of pK_a

acid	pK_a of acid	rel methanolysis rate[a]
CF_3SO_3H	-11	1.0
CF_3CO_2H	0.7	29
CH_3CO_2H	4.5	52

[a] Reactions were carried out by using 0.2 M TPB and 0.2 M MeOH and 0.02 M amounts of the respective acids in CCl_4 and were followed by IR.

Previous studies of protonolysis of trialkyl- or triarylborane compounds have revealed major differences in catalysis by protonic acids. In extended studies of protonolysis of $PhB(OH)_2$, Kuivila and co-workers showed that strong protonic acids catalyze B–C bond cleavage and that the rate of the reaction is directly proportional to $[H^+]$ concentration.[17] Dessey and Brown, on the other hand, have reported that protonolysis of Et_3B proceeds rapidly with weak acid catalysts such as carboxylic acids.[18,19] Dessey showed that the rate of protonolysis of Et_3B is inversely proportional to $[H^+]$ concentration. To determine whether TPB methanolysis more closely paralleled the protonolysis of $PhB(OH)_2$ or Et_3B, we briefly examined the dependence of methanolysis rate on $[H^+]$ concentration. The rate of methanolysis of TPB in CCl_4, catalyzed by the acids CF_3SO_3H, CF_3CO_2H, and CH_3CO_2H, was found to be inversely dependent on $[H^+]$ concentration, over a wide range in pK_a (Table IV). Thus, in close analogy with the conclusions of Dessey regarding formation of Et_2BOCOR,[18] carboxylic acid catalyzed methanolysis of TPB to form $Ph_2B(OMe)$ most likely involves rate-limiting Ph_2BOCOR formation.

^1H NMR was used to more accurately measure methanolysis rates by following decreases in the MeOH OH resonance with time (Figure 4). All solutions contained 0.02 M CF_3CO_2H as catalyst.[20]

A modified version of a computer program reported by Stabler and Chesnick was used to test various kinetic models for CF_3CO_3H-catalyzed methanolysis of TPB.[21] A good match between experimental and computer-generated rate data was obtained by using the following sets of reactions (Scheme I). The MeOH self-association equilibrium constants reported by Saunders were used.[5] The value of 316 for K_{equil} was assigned from the UV measurements of complexation between TPB and MeOH. The value of 0.13 for k_1 was chosen to make the overall rates of methanolysis, as determined by the computer and by experiment, comparable. Finally, the value of 10^3 for k_2 was chosen to make the methanolysis rate zero order with respect to MeOH concentration and to provide a kinetic way of stoichiometrically consuming MeOH.

Scheme I

$$\mathrm{MeOH} + \mathrm{MeOH} \rightleftarrows (\mathrm{MeOH})_2 \qquad K_1 = 0.6$$

$$(\mathrm{MeOH})_2 + \mathrm{MeOH} \rightleftarrows (\mathrm{MeOH})_3 \qquad K_2 = 3.8$$

$$(\mathrm{MeOH})_3 + \mathrm{MeOH} \rightleftarrows (\mathrm{MeOH})_4 \qquad K_3 = 28$$

$$\mathrm{TPB} + (\mathrm{MeOH})_3 \rightleftarrows \mathrm{TPB(MeOH)}_3 \qquad K_{\mathrm{equil}} = 316$$

$$\mathrm{TPB} + \mathrm{CF_3CO_2H} \rightarrow \mathrm{Ph_2BOCOCF_3} + \mathrm{C_6H_6} \qquad k_1 = 0.13$$

$$\mathrm{Ph_2BOCOCF_3} + \mathrm{MeOH} \rightarrow \mathrm{Ph_2B(OMe)} + \mathrm{CF_3CO_2H} \qquad k_2 = 10^3$$

Figure 5 shows a comparison of rates of methanolysis determined by the computer model with the corresponding rates measured by ^1H NMR. Although there is not absolute agreement in individual rates, the simulation of relative ordering from the fastest to the slowest rates is reasonable. A variety of alternate kinetic models was considered, including testing the above scheme for sensitivity to changes in the different rate and equilibrium constants, as well as several simplier schemes. Table V gives a summary of methanolysis rates determined for the four starting ratios of TPB and MeOH shown in Figure 5 for several different computer models. These calculated data show that poor simulations are obtained when either the MeOH self-association (entry 5) or the $TPB(MeOH)_n$

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[17] Kuivila, H. G.; et al. *J. Am. Chem. Soc.* **1961**, *83*, 2159 and earlier papers cited therein.

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[19] Brown, H. C.; Hebert, N. C. *J. Organomet. Chem.* **1983**, *255*, 135.

[20] It was not possible to record signals for MeOH conversion in the 0.2 M TPB/0.1 M MeOH and the 0.4 M TPB/0.1 M MeOH cases beyond about 15% and 31% conversion, respectively, because of peak degeneracies between OH and CH_3 resonances.

[21] Stabler, R. N.; Chesnick, J. *Int. J. Chem. Kinet.* **1978**, *10*, 461.

Table V. Comparison of Rates of Formation of PH_2BOMe Determined Experimentally by ^1H NMR and by Computer Simulation

entry	rate$_{rel}$ (dPh_2BOMe/dt) for $[TPB]_0/[MeOH]_0$ relative to 1 for $[TPB]_0/[MeOH]_0 = 0.4/1.0$			$(MeOH)_n$ self-assoc equilibria[a]	$TPB(MeOH)_n$ equilibria	
	0.4/0.4	0.2/0.2	0.2/0.1		n	K_{equil}
1[b]	0.60	0.33	0.44	+	3	316
2[b]	0.49	0.21	0.29	+	3	100
3[b]	0.70	0.34	0.47	+	3	500
4[b]	0.70	0.17	0.47	+	3	0
5[b]	0.15	0.07	0.36	–	1	300
6[c]	4.53	4.53	1.34	–	0	0
7[d]	1.0	0.5	0.5	–	0	0
8[e]	0.53	0.28	0.24			

[a] Equilibrium constants $K_2 = 0.6$, $K_3 = 3.8$, and $K_4 = 28$ taken from Table II. [b] Irreversible reactions included $TPB + CF_3CO_2H \xrightarrow{k = 0.13} Ph_2BOCOCF_3$; $MeOH + Ph_2BOCOCF_3 \xrightarrow{k = 10^3} Ph_2BOMe + CF_3CO_2H$. [c] Irreversible reaction was $TPB + MeOH \xrightarrow{k = 0.13} Ph_2BOMe$. [d] Irreversible reaction was $TPB \xrightarrow{k = 0.13} Ph_2BOMe$. [e] Measured by ^1H NMR (Figure 4).

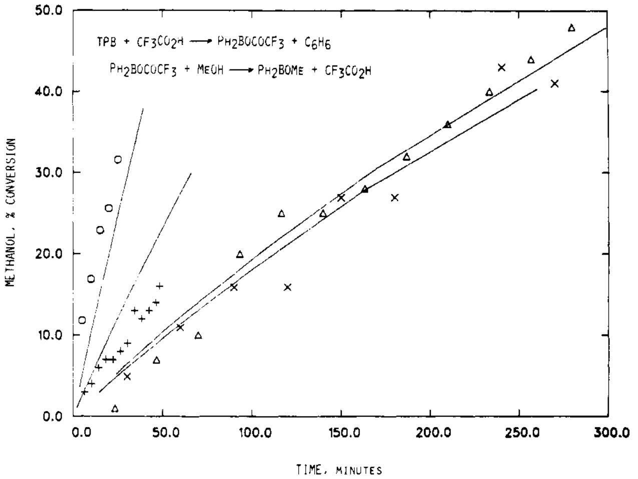

Figure 6. Comparison of methanol conversion rates determined by ^1H NMR (points) and by computer simulation (—). $TPB_0/MeOH_0$, M/M = 0.4/0.1 (○), 0.2/0.1 (+), 0.2/0.2 (×), 0.4/0.4 (△).

equilibria (entry 4), or both (entries 6 and 7) are excluded. The overall methanolysis reaction is best simulated by first-order dependence on TPB concentration and zero-order rate dependence on MeOH monomer concentration (entries 1, 2, 3, or 4). Attempts to make the reaction first order in MeOH concentration gave poorly predicted relative rates. For example, Figure 6 shows a plot of computer-simulated methanolysis reaction rates using the MeOH self-association equilibrium constants from Table II and a K_{equil} of 316 for $TPB(MeOH)_3$ formation used in Figure 5. The Ph_2BOMe formation step used in Figure 6, however, involved first-order dependence on MeOH as well as TPB ($TPB + MeOH + CF_3CO_2H \rightarrow Ph_2BOMe + CF_3CO_2H$). The rate of $Ph_2B(OMe)$ formation is moderately sensitive to the magnitude of K_{equil} for $TPB(MeOH)_3$ equilibrium (entries 2, 3, 4, and 5). The closest simulation of the ^1H NMR measured relative rates was achieved with K_{equil} for $TPB(MeOH)_3$ formation equal to 100 (entry 2) rather than 316 (entry 1). The important point is not the accuracy of the value assigned K_{equil}, but rather that complexation of TPB and MeOH occurs and does explain the apparent inverse order on MeOH concentration shown by the rate measurements by both IR and ^1H NMR (Figures 3 and 4).

Direct evidence was obtained for the formation of $Ph_2B(OCOCF_3)$, shown as the rate-limiting step (k_1). IR measurements were carried out in which CCl_4 solutions of TPB were treated with stoichiometric amounts of CF_3CO_2H or CH_3CO_2H. In both cases bands due to CO stretching modes (1760 and 1710 cm^{-1}, respectively) disappeared in agreement with formation of $Ph_2B(OCOR)$. Upon addition of equivalent amounts of MeOH, the CO stretching bands were restored, along with appearance of bands at 1325 cm^{-1}, assignable to the B–O–C band of $Ph_2B(OMe)$. In the case of acetic acid, the $Ph_2BOCOCH_3$ ester precipitates from CCl_4 solution on standing for about an hour. The ester was isolated from solution as a white solid and was characterized by IR and elemental analysis (see Experimental Section). The solution was distilled under vacuum and analyzed by IR and showed only the presence of benzene and CCl_4. When solid $Ph_2B(OCOCH_3)$ was treated with MeOH, $Ph_2B(OMe)$ was instantly formed. The good agreement between the rate data obtained by IR and ^1H NMR, in terms of relative ordering of ratios of TPB and MeOH from the fastest to the slowest reactions suggests that TPB and MeOH exhibit the same kinetic orders under both conditions. Thus, catalysis by either metal and acidic and basic impurities or by added CF_3CO_2H gives rise to $Ph_2B–X$ intermediates which form in rate-limiting steps to be followed by rapid reaction with MeOH to form $Ph_2B(OMe)$.

Experimental Section

Instrumentation. ^1H and ^{13}C NMR spectra were recorded on a Nicolet NMC360WB spectrometer. ^{11}B NMR spectra were recorded on a Bruker HFX90 NMR spectrometer. A Perkin-Elmer 1420 spectrophotometer was used for IR measurements. A Du Pont 840 HPLC instrument was used, with a C-18 column in isocratic mode, to separate Ph_2BO-*i*-Pr from TPB. Measurements by UV spectroscopy were done with a Perkin-Elmer 559 UV–vis instrument. ESR measurements were made on a Bruker ER420 spectrometer. All measurements were done at room temperature.

Materials and Procedures. All solutions containing TPB were prepared and transferred in a Vacuum Atmospheres Inc. N_2-filled inert atmosphere glovebox to avoid contamination with air or moisture. All solvents and alcohols were reagent grade and were degassed of air by N_2 sparging and were dried by storing over 3-Å molecular sieves which were activated by heating under vacuum at 250 °C overnight. TPB was obtained from Orgmet Co. and was purified by twice recrystallizing from acetonitrile. Metal wires and metal oxides were obtained from Morton Thiokol, Inc., Alfa Products Division. The wires had purities of at least 99.99% based on metal content with diameters ranging from 0.05 mm to 0.25 mm. Metal oxides were all ultrapure grade powders with the following surface areas in m^2/g: Al_2O_3 (118), CuO (3.1), Fe_2O_3 (13.4), NiO (4.8), and ZnO (0.3).[22]

Reaction of TPB with CH_3CO_2H and CF_3CO_2H. Reactions of TPB with CH_3CO_2H and with CF_3CO_2H in CCl_4 solution were followed by IR. Because TPB reacts more readily with CH_3CO_2H than with CF_3CO_2H, and because $Ph_2BOCOCH_3$ precipitated from CCl_4 solution (in the absence of alcohols), the following reactions are described to illustrate features of the reactions of TPB with carboxylic acids in general. A CCl_4 solution containing 0.2 M TPB

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[22] Surface area measurements were made by a N_2 absorption technique by E. E. Carroll.

was treated with 0.1 M CH_3CO_2H. When analyzed by IR after 50 min, the C=O band of CH_3CO_2H (1710 cm^{-1}) was absent and the solution was water-white. After an additional 10 min, a white precipitate ($Ph_2BOCOCH_3$) formed. Two equivalents of MeOH (0.2 M) were added and the mixture was shaken. The white solid quickly dissolved. IR analysis of the resulting solution revealed a strong band at 1710 cm^{-1} (CH_3CO_2H) and a new strong band at 1325 cm^{-1} assigned to Ph_2BOMe. Proof that the white precipitate was the mixed anhydride, and not simply a TPB(MeOH) complex, was obtained by isolation of the white precipitate obtained in the reaction of 0.050 g of TPB (0.2 M) with 11.4 μL (0.2 M) of CH_3CO_2H in 1 cc of CCl_4. The KBr IR spectrum of the precipitate showed a weak broad band at 1720 cm^{-1}, assigned to the C=O group of $Ph_2BOCOCH_3$. The solvent was vacuum stripped and was analyzed by IR which showed peaks assigned to benzene (1475, 1805, 1950, 3015, and 3040 cm^{-1}), in addition to peaks from CCl_4 and a trace of CH_3CO_2H. The assignment of the structure $Ph_2BOCOCH_3$ for the white precipitate was also confirmed by ^1H NMR analysis. The aromatic protons (δ 7.75) and CH_3 protons (δ 2.2) gave an integral ratio 3.9/1 (theoretical 3.3). Finally, elemental analysis of the solid gave results more in agreement with the assigned mixed anhydride structure rather than a simple $TPB(CH_3CO_2H)$ complex. Anal. Calcd for $Ph_2BOCOCH_3$, $C_{14}H_{13}BO_2$: C, 75.00; H, 5.80. Found: C, 72.56 ± 1.23; H, 5.53 ± 0.12. Calcd for $TPB(CH_3CO_2H)$, $C_{20}H_{22}BO_2$: C, 78.69; H, 7.21.

Reaction of TPB with MeOH, Catalyzed by Metals and Metal Oxides. A stock solution was prepared which contained 0.2 M TPB and 0.2 M MeOH in CCl_4. Aliquots of 0.5 mL were placed in a series of small glass vials containing coils of metal wires, with diameters ranging from 0.05 mm to 0.25 mm, and of sufficient lengths to give surface areas of 0.4 cm^2. The wires included Al, Zn, Fe, Ni, and Cu. Analyses of the solutions by IR after 17 to 20 h showed that about 1% conversion of the MeOH per hour had taken place in the vials containing Al, Fe, and Ni wires as well as in the stock solution not exposed to metal. The solutions containing Zn and Cu metal, however, gave about 4% and 2% conversion per hour of MeOH. Very similar results were obtained when the experiments were repeated in toluene solvent. The percent MeOH conversions per hour were: Al (2%), Zn (3.5%), Fe (1.5%), Ni (2%), Cu (3.5%), and the control with no metal (2%). Possible catalysis by metal oxides was examined by repeating the experiments and using 0.01-g amounts of metal oxides in place of the metal wires. The percent MeOH conversions per hour were: Al_2O_3 (0%), Zn (1%), Fe_3O_4 (0%), NiO (0%), CuO (3%), and the control with no metal oxide (0%).

Computer Kinetic Model Calculation of $TPB(MeOH)_3$/TPB Ratios. The equations used to calculate rates of CF_3CO_2H methanolysis of TPB were also used to calculate percentages of $TPB(MeOH)_3$ and free TPB. For these cases, the irreversible rate constants k_1 and k_2 were set to zero. The three equilibrium rate constants for self-association of MeOH (K_1, K_2, and K_3) were set to 0.6, 3.8, and 28, respectively. The K_{equil} for $TPB(MeOH)_3$ formation was set to 316. For the ^{11}B NMR measurement conditions, with 0.32 M $[TPB]_{total}$ and 1.0 M $[MeOH]_{total}$ in Freon-11, the computer equilibrium ratio was 0.227 M $TPB(MeOH)_3$/0.0935 M TPB, or 70.8/29.2. For the ^{13}C NMR measurement conditions, with 0.20 M $[TPB]_{total}$ and 24.7 M $[MeOH]_{total}$ (neat MeOH), the computer equilibrium ratio was 0.199 M $TPB(MeOH)_3$/0.0017 M TPB, or 99.1/0.9.

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Registry No. TPB, 960-71-4; $Ph_2B(MeO)$, 13471-36-8; $PhB(OMe)_2$, 13471-35-7; $Ph_2B(OEt)$, 43185-52-0; $PhB(OEt)_2$, 31044-59-4; $B(OMe)_3$, 121-43-7; $B(OEt)_3$, 150-46-9; MeOH, 67-56-1; EtOH, 64-17-5; *t*-BuOH, 75-65-0; $Ph_2B(O\text{-}t\text{-}Bu)$, 958-03-2; *i*-PrOH, 67-63-0; $Ph_2B(O\text{-}i\text{-}Pr)$, 69737-51-5; CF_3SO_3H, 1493-13-6; CF_3CO_2H, 76-05-1; CH_3CO_2H, 64-19-7; $Ph_2B(OCOCH_3)$, 93757-49-4; $Ph_2B(OCOCF_3)$, 3826-41-3; Zn, 7440-66-6; Cu, 7440-50-8.

Ene Reactions of Conjugated Dienes. 2. Dependence of Rate on Degree of Hydrogen Removed and s-Cis or s-Trans Diene Character

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The rates of the ene reactions between diethyl diazenedicarboxylate and a number of dienes have been measured and product structures determined. Accelerated reactions are observed with 1,3-cyclohexadienes but not with dienes held fixed in the s-trans form. Within the first set of systems tertiary hydrogens are much more reactive than secondary. Within the second set secondary are (in turn) more reactive than primary. There is no apparent correlation between the rate of the Diels–Alder reaction of the 1,3-cyclohexadienes with maleic anhydride and the rate of ene reaction with the diazenedicarboxylate.

Certain conjugated dienes have been observed to undergo facile ene reactions, even when the Diels–Alder reaction might well be expected to overwhelm them.[1] In an earlier paper,[2] acceleration of the ene reactions of dienes 1 and 2 was demonstrated, rather than a previously hypothesized slowing of the competing Diels–Alder process.[3] However, the generality of this was unclear. We have extended this earlier work, first to ascertain how general such acceleration is and then whether acceleration is a consequence of mere conjugation, of the endocyclic nature (i.e., s-cis conformation) of these dienes, or of the greater rigidity and likelihood of having an appropriately aligned hydrogen that results from placing the diene in a ring. It was also felt desirable to test the earlier inference that the observed transfer of hydrogen from the more substituted allylic position was to be expected in other cases[2] in contrast to the opposite preference found with simple alkenes.[4]

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