crystalline precipitate with the aid of a hypodermic syringe. Distillation of the solvent gave 19.6 g (95%) of methyl dicyclohexylborinate.[13] The treatment of methyl dialkylborinates with another alcohol results in the displacement of methanol and the formation of the corresponding alkyl ester of dialkylborinic acid in quantitative yield.

A number of representative reactions involving the conversion of trialkylboranes into the corresponding dialkylborinic acids and esters are given in Table I.[13]

Table I. The Synthesis of Dialkylborinic Acids and Their Alkyl and Aryl Esters from Trialkylboranes *via* Redistribution with *o*-Tolyl Borate

Dialkylborinic acid derivative R_2BOR'		Yield, %[a]		Bp,	
R	R′	Glpc	Isol	°C (mm)	$n^{20}D$
Isobutyl	Phenyl	90			
Isobutyl	2,6-Dimethylphenyl	94			
Isobutyl	*o*-Tolyl	92	84	75 (0.25)	1.4750
1-Butyl	Phenyl	90	80	120 (10)	1.4770[b]
1-Butyl	*o*-Tolyl	90	80	78–80 (0.2)	1.4765
2-Butyl	*o*-Tolyl	92	81	67–68 (0.15)	1.4790
Cyclopentyl	*o*-Tolyl	91	85	118 (0.3)	1.5160
Cyclohexyl	*o*-Tolyl		90	150 (0.25)	1.5210
exo-Norbornyl	*o*-Tolyl		84	140–142 (0.1)	1.5405
1-Butyl	8-Quinolinyl		98	152 (0.3)	1.5735
Isobutyl	8-Quinolinyl		95	136 (0.25)	1.5730
2-Butyl	8-Quinolinyl		94	155 (0.35)	1.5805
Cyclohexyl	8-Quinolinyl		90	126–130[c]	
1-Butyl	Methyl	97[d]		55–56 (5)	1.4145[e]
Isobutyl	Methyl	98[d]		45–46 (8)	1.4080
2-Butyl	Methyl	99[d]		48–50 (6)	1.4175
Cyclohexyl	Methyl		95[d]		
1-Butyl	Hydrogen		95[d]	84 (0.25)	1.4280[f]
Cyclohexyl	Hydrogen		95[d]	52[g]	

[a] Unless indicated otherwise, the products were obtained by the redistribution method. [b] B. M. Mikhailov, V. A. Vaver, and Yu N. Bubnov (*Dokl. Akad. Nauk SSSR*, **126,** 575 (1959)) report bp 118–119° (7 mm); $n^{20}D$ 1.4760. [c] Melting point of the compound. [d] Prepared from the corresponding 8-quinolinyl ester. [e] Lit.[9] bp 55–57° (8.0 mm); $n^{20}D$ 1.4145. [f] Isolated as di-*n*-butylborinic anhydride. M. F. Hawthorne and M. Reintjes (*J. Org. Chem.*, **30,** 3851 (1965)) report bp 82–84° (0.1 mm); $n^{20}D$ 1.4277. [g] Lit.[15] mp 55°.

Consequently, there is now available, for the first time, a simple synthetic route to dialkylborinic acids and esters which appears generally applicable, even to derivatives which cannot be distilled.

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The Temperature Dependence of the Photochemical Addition of *trans*-Stilbene to Olefins

Sir:

Evidence has been presented that the photochemical addition of *trans*-stilbene to tetramethylethylene (TME) involves addition of ^{1}S *trans*-stilbene to tetramethylethylene *via* an exciplex.[1] While the inverse temperature dependence of k_{app} was interpreted as evidence for reversible exciplex formation, the treatment given ignored the temperature effect on the lifetime of ^{1}S *trans*-stilbene. We therefore wish to correct the previously reported k_{app} values for variations in the singlet lifetime of stilbene and present new data which clearly illustrate the magnitude of this inverse temperature dependence.

Dyck and McClure[2] and Malkin and Fischer[3] independently observed the variation in τ with temperature; their results show that an activated process leading to cis–trans isomerization competes with stilbene fluorescence. This temperature-dependent step has been subsequently identified with formation of the twisted stilbene singlet (^{1}p) from which isomerization occurs.[4,5] Before determining the temperature dependence of the rate constant for adduct formation, it is necessary to take into account variations in the lifetime of ${}^1t$ with temperature.

The Arrhenius equation derived by Dyck and McClure[2] has been applied to the fluorescence quantum yields of Malkin and Fischer.[3,6] Assuming a temperature-independent fluorescence rate constant of 4×10^8 sec^{-1},[2] the temperature dependence of the rate constant for the process leading to cis–trans photoisomerization, eq 1, is given by eq 2,[6] where $A = 5.6 \times 10^{11}$ sec^{-1} and

$$ {}^1\text{t} \xrightarrow{k_1} {}^1\text{p} \tag{1} $$

$$ k_1 = Ae^{-E_a/RT} \tag{2} $$

$E_a = 2.84$ kcal/mol.[7]

The simplest mechanism which can account for the cycloaddition reaction is given by eq 3–7. Intersystem

$$ {}^0\text{t} \xrightarrow{h\nu} {}^1\text{t} \tag{3} $$

$$ {}^1\text{t} \xrightarrow{k_1} {}^1\text{p} \tag{4} $$

$$ {}^1\text{t} \xrightarrow{k_2} {}^0\text{t} + h\nu \tag{5} $$

$$ {}^1\text{t} + \text{TME} \xrightarrow{k_3} \text{adduct} \tag{6} $$

$$ {}^1\text{p} \xrightarrow{k_4} \alpha{}^0\text{t} + (1 - \alpha){}^0\text{c} \tag{7} $$

crossing, ${}^1\text{t} \rightarrow {}^3\text{t}$, is not included since we estimate that its rate constant has a maximum value of $\sim 0.1k_2$.[5] Using the steady-state approximation for excited state species eq 8 may be derived, where $\tau = (k_1 + k_2)^{-1}$.

$$ \phi_{\text{add}}^{-1} = 1 + (\tau k_3[\text{TME}])^{-1} \tag{8} $$

This equation is analogous to the one derived for the first mechanism in ref 1 and describes the dependence of the quantum yield of adduct formation on the concentration of tetramethylethylene.

Slopes of ϕ_{add}^{-1} *vs.* $[\text{TME}]^{-1}$ at various temperatures give $(\tau k_3)^{-1}$ from which it is possible to determine k_3. The τ values predicted for these temperatures were calculated using $\tau = (k_1 + k_2)^{-1}$ with $k_2 = 4 \times 10^8$ sec^{-1} and k_1 obtained from eq 2. Table I shows values of k_3

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[1] O. L. Chapman and R. D. Lura, *J. Amer. Chem. Soc.*, **92,** 6352 (1970).

[2] R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36,** 2326 (1962).

[3] S. Malkin and E. Fischer, *J. Phys. Chem.*, **66,** 2482 (1962); **68,** 1153 (1964).

[4] J. Saltiel, *J. Amer. Chem. Soc.*, **90,** 6394 (1968).

[5] J. Saltiel and E. D. Megarity, *ibid.*, **91,** 1265 (1969).

[6] E. D. Megarity, Ph.D. Thesis, The Florida State University, 1969.

[7] Dyck and McClure's fluorescence data give $A = 1.1 \times 10^{12}$ sec^{-1} and $E_a = 3$ kcal/mol,[2] while treatment of the temperature dependence of $\phi_{t \rightarrow c}$ reported by Malkin and Fischer[3] gives $A = 2.6 \times 10^{11}$ sec^{-1} and $E_a = 2.5$ kcal/mol.

Table I. Kinetic Parameters for the Photochemical Addition of *trans*-Stilbene to Tetramethylethylene

T, °C	Slope, M	$\tau \times 10^{10}$, sec	$k_3 \times 10^{-9}$, M^{-1} sec^{-1}
54	8.06	1.33	0.93
44	7.00	1.52	0.94
34	5.88	1.74	0.98
25	4.20	1.98	1.20
5	2.94	2.70	1.33
−5	1.34	3.23	2.52
−10	0.94	3.50	4.47
−22	0.28	4.42	8.10

for a greater range of temperatures than that previously available. The values of k_3 given in Table I ignore any temperature effects on diffusion which would operate in the opposite direction. Inclusion of these effects would enhance the negative temperature dependence of k_3. If the temperature effect on the lifetime of ^{1}S *trans*-stilbene were the only temperature effect on the addition, k_3 should be constant and all olefins should show the same temperature dependence. This is not the case. It is clear that k_3 has a negative temperature dependence. Table II shows k_3 values for the addition of *trans*-stilbene to 1-methylcyclohexene.[8] The negative temperature dependence is observed in this case as well. Furthermore, comparison of the ratios of the slopes at the extreme temperatures for tetramethylethylene (28.5) and 1-methylcyclohexene (5.3) shows that the temperature dependence for addition to these two olefins is not the same. Although a quantitative treatment of this temperature dependence indicates that the above mechanism is incomplete (*i.e.*, at least one more activated process must be available to the exciplex), the observed negative temperature dependence of k_3 is consistent with reversible exciplex formation as suggested in ref 1. Expansion of eq 3 to include reversible exciplex formation (eq 9 and 10) gives k_3 =

Table II. Kinetic Parameters for the Photochemical Addition of *trans*-Stilbene to 1-Methylcyclohexene

T, °C	Slope, M	$\tau \times 10^{10}$, sec	$k_3 \times 10^{9}$, M^{-1} sec^{-1}
56	156	1.29	4.74
43	134	1.54	4.86
34	108	1.74	5.37
25	89.4	1.98	5.67
−21	29.4	4.33	8.14

$$ {}^1\mathrm{t} + \mathrm{O} \overset{k_e}{\rightleftarrows} \text{exciplex} \qquad (9) $$

$$ \text{exciplex} \xrightarrow{k_a} \text{adduct} \qquad (10) $$

$k_e[k_a/(k_a + k_{-e})]$. The expression $k_e[k_a/(k_a + k_{-e})]$ is the product of the rate constant for exciplex formation and the fraction of exciplex which gives adduct.[1]

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(8) The product of the addition of *trans*-stilbene to 1-methylcyclohexene is 1-methyl-7,8-diphenylbicyclo[4.2.0]octane. The mass spectrum shows the parent ion at *m/e* 276 and the base peak at *m/e* 180 (stilbene). The nmr spectrum (CCl_4) shows a singlet at δ 7.11 (10 H, aromatic protons), a multiplet at 3.2–4.2 (2 H, benzylic protons), a multiplet at 0.80–2.50 (9 H, methylene and methine protons), and a singlet at 0.88 (3 H, methyl protons).

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Supramolecular Bonding Orbitals from Molecular Antibonding Orbitals. Structure of the Radical Anion of Sulfuryl Chloride[1]

Sir:

Just as atomic orbitals are used to obtain molecular orbitals, so molecular orbitals can be combined to form supramolecular orbitals. Of particular interest here is the combination of two *antibonding* orbitals from separate molecules, which gives rise to a supramolecular *bonding* orbital between the molecules. Application of this proposition suggests that a radical anion may enter into chemical combination with a neutral molecule in a geometrical configuration which permits the antibonding orbitals to have positive overlap.

Molecules with low-lying vacant orbitals frequently undergo electron capture during γ irradiation,[2] and this method has been used to generate $SO_2Cl_2\cdot^-$. We find that the esr spectrum of this species can be most satisfactorily interpreted according to a novel structure in which the unpaired electron resides in a supramolecular bonding orbital derived from a combination of the lowest unoccupied antibonding orbitals of individual SO_2 and Cl_2 molecules.

Figure 1 shows the esr spectrum of γ-irradiated polycrystalline SO_2Cl_2 at 77°K. Much of the hyperfine structure inside the hydrogen-atom lines is typical of a radical with an axially symmetric hyperfine tensor. The parallel features of this anisotropic (powder) spectrum are clearly attributable to interaction with two equivalent chlorine nuclei and the outermost lines due to the $^{35}Cl^{35}Cl$ and $^{35}Cl^{37}Cl$ species are particularly well resolved. From the positions of these lines we obtain the values $A_{\|}^{35}$ = 64.1 G, $A_{\|}^{37}$ = 53.3 G, and $g_{\|}$ = 2.0050. The perpendicular features are not readily distinguished, but they must lie inside the $m_I = -1$ and $m_I = +1$ parallel components and limits of 0 and 16 G can be set for $A_{\perp}^{35}$. This large degree of anisotropy was verified qualitatively by experiments on samples exhibiting preferential orientation. In none of these experiments with aligned samples did the total width of the spectrum exceed that of the polycrystalline spectrum, and at orientations close to the parallel direction, there was a marked collapse in the spectral width on rotation of the sample through an angle of 90°. If $A_{\|}$ and $A_{\perp}$ are both assumed to be positive, the above values lead to the limits a_{iso} =

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(2) D. J. Whelan, *Chem. Rev.*, **69**, 179 (1969).