If the step

$$^3P_0 + Q \longrightarrow \text{removal} \qquad k_6$$

is added to the mechanism to explain the quenching by added molecules Q, then a steady-state treatment predicts that $\tau_0/\tau = 1 + k_6\tau_0[Q]$, where τ_0 and τ are the lifetimes in the absence and presence of the quencher. This relation is in agreement with the experimental results, and so the proposed mechanism is sufficient to explain the experimental behavior. The rate constants (M^{-1} sec^{-1}) for the quenching of triplet pentanedione by acrolein, crotonaldehyde, and methyl vinyl ketone at various temperatures (°C) are shown in Table I.

Table I. Rate Constants for Quenching of Triplet 2,3-Pentanedione

Acrolein	Crotonaldehyde	Methyl vinyl ketone
3.8×10^4 at 42.2°	4.6×10^5 at 60.2°	6.8×10^4 at 62.5°
1.1×10^5 at 50.8°	1.0×10^6 at 71.5°	1.1×10^5 at 70.8°
1.5×10^5 at 68.3°	1.6×10^6 at 84.4°	1.5×10^5 at 80.5°
5.5×10^5 at 88.3°		

For each of the compounds the quenching efficiency increases with temperature and is of the Arrhenius form. The data for crotonaldehyde yield $k_6 = 10^{13.8\pm1.5}e^{-(12.4\pm2.4)/RT}$ and for methyl vinyl ketone $k_6 = 10^{11.7\pm1.0}e^{-(10.4\pm1.5)/RT}$. A weighted least-squares treatment of the acrolein data gives $k_6 = 10^{14.0\pm1.5}e^{-(13.7\pm2.1)/RT}$. The errors in the preexponential factors and activation energies are large because only a short temperature range is accessible experimentally. At low temperature the quenching molecules have low vapor pressures and there is only a small effect on the triplet lifetime. At high temperature the triplet diketone has a very short lifetime and again only a small effect of quencher can be observed. Although the quenching rate constant is not large, it is unlikely that impurity in the quencher could explain the observations; that would entail an unrealistically high value for the preexponential factor.

The quenching behavior is followed by its effect on the phosphorescence lifetime so that only the interaction of the triplet state of pentanedione and the quencher need be considered. The quenching process could involve either a chemical interaction or an endothermic energy transfer to form the triplet state of the quencher.

The energy of the triplet state of 2,3-pentanedione is about 55 kcal,[8] but the energies of the unsaturated carbonyl compounds are less certain. It has been suggested[9,10] that the energy of the π^*,n triplet state of acrolein is about 69 kcal, and there is a report that the triplet energy of crotonaldehyde is similar.[11] The triplet energy of methyl vinyl ketone is not available. It has been suggested,[12] however, that the energy of the triplet state of acetone is lower than that of acetaldehyde. The triplet energy of methyl vinyl ketone could be lower than that of acrolein; this would be necessary if the quenching process involves energy transfer. If triplet states of the quenching are formed in the system then reverse energy transfer from the triplet state of the quencher to the ground state of the diketone could complicate the kinetics. Separate experiments, however, showed that reverse transfer is improbable.

An alternative explanation of the data is that the chemical interaction of the triplet state of the diketone and the ground state of the quencher involves an activation energy. There are no experiments reported of the photolysis of simple α-diketones in the presence of enones, but products have been isolated from the photolysis in solution of a complex α-diketone in the presence of dienes.[13] The preexponential factors for the quenching process are larger than might be expected, but a large value was also noted[8] in the self-quenching process Thus a chemical interaction between the triplet state of the diketone and the ground state of the enone is also possible.

In conclusion, the above data show that the processes removing the triplet state of 2,3-pentanedione change with temperature and that certain quenching processes can have significant activation energies. Further research is planned to decide between quenching by energy transfer and chemical reaction.

Acknowledgments. We thank the National Research Council of Canada for financial support.

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Received January 9, 1971

The Facile Redistribution of Trialkylboranes with Aryl Borates. A General Synthesis of Dialkylborinic Acids and Esters

Sir:

Trialkylboranes undergo a facile redistribution with aryl borates, under the catalytic influence of borane in THF, forming the corresponding dialkylborinic esters in nearly quantitative yield (eq 1). Since the equilibrium

$$2R_3B + B(OAr)_3 \xrightarrow[100°]{\text{cat. } H_3B\text{-THF}} 3R_2BOAr \qquad (1)$$

goes essentially to completion, the crude reaction product can often be utilized directly. Alternatively, the crude reaction products are readily converted to relatively stable, easily handled 8-hydroxyquinolinates. These are easily purified and converted to the corresponding free acids or methyl esters. Consequently, it now becomes possible to synthesize a wide range of dialkylborinic acids and esters not previously available because of their instability toward the distillation conditions required to isolate them from the redistribution reaction mixtures.

Dialkylborinic acids and esters are now finding important applications in the new chemistry of organoboranes. Thus, the reduction of methyl dialkylborinates with lithium aluminum hydride in the presence of olefins provides a convenient synthesis of mixed organoboranes, R_2BR'.[1] The reduction of these esters with aluminum hydride makes available the dialkylboranes.[2] Similarly, the bromination of dialkylborinic acids in the presence of water[3] provides a promising new route to secondary alcohols.[4]

These developments have made it desirable to have a simple general synthesis of dialkylborinic acids and esters. Unfortunately, the yields are often low in the reaction of organometallic reagents with borate esters.[5] Selective protonolysis of trialkylboranes with acetyl acetone[6] or a thiol[7] is more favorable, but requires the immediate loss of one of the three alkyl groups on boron.

This disadvantage could conceivably be circumvented by adoption of a redistribution procedure[8] (eq 2). Investigation revealed that the procedure was rela-

$$2R_3B + B(OCH_3)_3 \xrightarrow[100°]{H_3B\text{-}THF} 3R_2BOCH_3 \qquad (2)$$

tively satisfactory for the organoboranes from terminal, straight-chain olefins, but was less satisfactory for trialkylboranes from α-branched terminal olefins, such as isobutylene, internal olefins, such as 2-butene, and cyclic olefins, such as cyclopentene and cyclohexene. These derivatives underwent a slow, relatively incomplete redistribution. Isolation of the desired borinic ester from the equilibrium mixtures could be achieved by distillation. However, this was satisfactory only for the more volatile derivatives. Less volatile borinic esters, such as methyl dicyclohexylborinate, tend to disproportionate on distillation.[9]

It was discovered that substitution of the methyl borate by aryl borates gave a much more rapid redistribution, complete in all cases in 2–6 hr at 100°. Moreover, in all cases examined the reactions proceeded far toward completion, giving 90–94% of the desired dialkylborinates. Because of its physical characteristics, *o*-tolyl borate was adopted as the preferred reagent.

The fact that the reaction proceeds so far to completion, makes it possible to utilize the crude reaction product directly for many applications. The synthesis of diisobutyl-*n*-pentylborane from triisobutylborane will be illustrative of this synthetic convenience. A mixture of triisobutylborane (1.82 g, 10 mmol), *o*-tolyl borate[10] (1.65 g, 5 mmol), and borane in THF (0.5 mmol) was stirred under nitrogen at 100° for 2 hr.[11] After cooling, pentane (15 ml) was added to it followed by 1-pentene (1.2 g, 17 mmol) and lithium aluminum hydride in ethyl ether (3.4 ml of 1.5 *M*, 5.1 mmol) at 0°. After stirring for 30 min at that temperature, ice-cold sodium hydroxide solution (20 ml of 3 *N*, 60 mmol) was added. After stirring for 5 min, glpc analysis of the supernatant organic phase indicated the presence of diisobutyl-*n*-pentylborane[1] in 85% yield.

In the case of more volatile derivatives, it is possible to isolate and purify the product by distillation. Thus, *o*-tolyl diisobutylborinate, bp 75° (0.25 mm), was isolated in 84% yield, and gave diisobutyl-*n*-pentylborane[1] in a yield of 100% and a purity of 94%, when treated with lithium aluminum hydride in the presence of 1-pentene. The *o*-tolyl dialkylborinates can be conveniently converted to the corresponding borinic acid by the following procedure. A mixture of *o*-tolyl dicyclopentylborinate (2.56 g, 10 mmol), glycerol (0.92 g, 10 mmol), and ethylene glycol (1.24 g, 20 mmol) was heated at 100° removing the liberated *o*-cresol and excess ethylene glycol at 0.2 mm. The residue, presumably the glycerol ester of dicyclopentylborinic acid, was then stirred with water (5 ml) and hexane (10 ml) for 30 min at 25°, giving a hexane solution of dicyclopentylborinic acid in essentially quantitative yield.

In the case of the less volatile derivatives, where distillation of the *o*-tolyl dialkylborinates may be impractical, conversion to 8-hydroxyquinolinates[12] provides a more satisfactory means of isolating and purifying the dialkylborinic acids. The transformation of tricyclohexylborane into 8-quinolinyl dicyclohexylborinate is a representative example. Tricyclohexylborane (13.0 g, 50 mmol) and *o*-tolyl borate (8.3 g, 25 mmol) were stirred together under the blanket of nitrogen at 100° in the presence of borane in THF (2.5 mmol) for 6 hr.[11] After cooling, methanol (10 ml) and 8-hydroxyquinoline (11.3 g, 75 mmol) were added to it. The resulting yellow solution was stirred for 15 min and then diluted with water. The yellow solid obtained was recrystallized from acetone–water to give 21.6 g (90%) of pure product; mp 126–130°.[13]

These 8-hydroxyquinolinates are readily converted to the free acids or into the corresponding methyl esters, as shown by the following procedures. A mixture of 8-quinolinyl dicyclohexylborinate (3.2 g, 10 mmol), water (10 ml), and sulfuric acid (96%, 5.0 g, 50 mmol) was refluxed under nitrogen for 1 hr. Hexane (50 ml) was then added to it and the mixture was cooled after rapid stirring for 5 min. The organic layer was subsequently separated from the crystalline precipitate and washed with brine. The removal of the solvent provided 1.84 g (95%) of dicyclohexylborinic acid; mp 52° (lit.[14] mp 55°). Similarly, 8-quinolinyl dicyclohexylborinate (32.1 g, 100 mmol) was dissolved in dry methanol (50 ml) and then 100% sulfuric acid (9.8 g, 100 mmol) was added to it with stirring under nitrogen at 25–30°. The resulting yellow solution was stirred for 15 min, and then diluted with pentane (200 ml) and cooled. The organic layer was then separated from the

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(11) The redistribution was complete in 2 hr in the case of trialkylboranes from terminal alkenes, whereas a 4–6-hr heating period was required in the case of those from internal and cyclic olefins.

(12) The preparation of 8-quinolinyl diaryl- and alkylarylborinates has been described (J. E. Douglass, *J. Org. Chem.*, **26**, 1312 (1961)). However, these compounds could not be hydrolyzed to the corresponding borinic acids even after prolonged treatment with hot dilute mineral acid.[5]

(13) All the compounds were analyzed by ir and nmr spectroscopy. All the new compounds also gave concordant elemental analyses.

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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.

(15) Postdoctorate research associate on funds provided by the National Institutes of Health (Grant No. GM-10937).

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Received March 22, 1971

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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