TABLE I

Compound	Position of CH_2	Signal	Chemical shift, ppm	$W_{h/2}$,[a] cps
3α,3′ epoxide[b]	Equatorial	Singlet	2.40	0.40 ± 0.05
3β,3′ epoxide[b]	Axial	Singlet	2.34	1.37 ± 0.09
6α,6′ epoxide[b]	Axial	Quartet	2.28	1.35 ± 0.02
			2.36	1.41 ± 0.05
			2.50	2.16 ± 0.05
			2.58	2.14 ± 0.07
6β,6′ epoxide[b]	Equatorial	Quartet	2.03	0.81 ± 0.07
			2.11	0.90 ± 0.06
			2.56	1.00 ± 0.05
			2.63	0.94 ± 0.05
7α,7′ epoxide[b]	Equatorial	Quartet	2.11	1.06 ± 0.06
			2.18	1.07 ± 0.08
			2.97	1.46 ± 0.05
			3.04	1.36 ± 0.03
7β,7′ epoxide[b]	Axial	Quartet	2.13	1.16 ± 0.04
			2.21	1.27 ± 0.04
			2.58	3.20 ± 0.06
			2.66	3.20 ± 0.03
12α,12′ epoxide[c]	Equatorial	Quartet	2.43	1.05 ± 0.08
			2.51 2.54	Peaks merged
			2.61	1.20 ± 0.09
12β,12′ epoxide[c]	Axial	Quartet (?)	2.40	0.96 ± 0.04
			2.47	0.99 ± 0.06
			2.93 2.96	3.48 ± 0.05
			3.00 3.03	3.50 ± 0.05

[a] $W_{h/2} = (CH_2O)_{h/2} - (TMS)W_{h/2}$. The average deviation is that for the experimentally measured $W_{h/2}$. All spectra were measured on a Varian A-60 spectrometer at a 0.2-cps sweep time, 50-cycle sweep width, a filter band width of 4, and radiofrequency field setting of 0.04. [b] The samples were 20% w/v in carbon tetrachloride containing 1% TMS. [c] The samples were 20% w/v in chloroform containing 1% TMS.

The additional coupling of the downfield proton for the pseudoaxial epoxide methylene group in the 12β,12′ epoxide is reflected in the appearance of the downfield proton as a poorly resolved quartet.

Registry No.—3α,3′ epoxide, 18744-05-3; 3β,3′ epoxide, 18744-06-4; 6α,6′ epoxide, 18744-07-5; 6β,6′ epoxide, 18744-08-6; 7α,7′ epoxide, 18744-09-7; 7β,7′ epoxide, 18744-10-0; 12α,12′ epoxide, 4965-90-6; 12β,12′ epoxide, 4965-91-7.

The Cycloaddition of Diphenylketene to 2-Vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane

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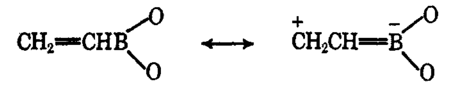
The interest in cycloaddition reactions of ketenes has recently received attention in regard to mechanism.[2-6] Since there have been no reports of electrophilic olefins[7] undergoing a cycloaddition reaction to diphenylketene, we thought it of interest to study the cycloaddition of diphenylketene to a vinylborono compound.



Vinylborono compounds are unusual in that a partial delocalization of the π electrons to a vacant 2p orbital is opposed by an electron-donating inductive effect.[8] Thus diphenylketene and 2-vinyl-4,4,6-trimethyl-1,3,-2-dioxaborinane (VTDB)[9] were heated at 110° for 360 hr to give a 26% yield of 2-(2′,2′-diphenylcyclobut-3′-on-1′-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (1) (eq 1).

Compound 1 had the characteristic infrared absorption of a cyclobutanone carbonyl at 5.63 μ (Nujol). The nmr spectrum of 1 (CCl_4, TMS) gave the typical AB portion of an ABX spectrum which consisted of two overlapping quartets[10] centered at τ 7.05 (a, b) ($J_{ab} = -17.0$ cps, $J_{ac} + J_{bc} = 24$ cps) whose coupling constants and chemical shifts were consistent with those pre-

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[2] J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 26 (1962).

[3] R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **28**, 1468 (1963).

[4] J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *ibid.*, **30**, 4175 (1965).

[5] W. T. Brady and H. R. O'Neal, *ibid.*, **32** 612 (1967).

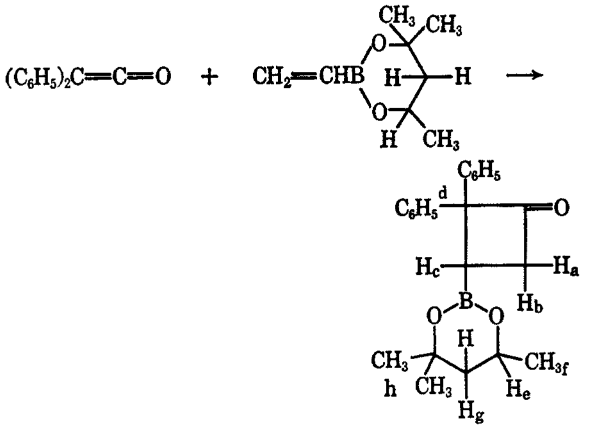
[6] T. J. Katz and R. Dessau, *J. Amer. Chem. Soc.*, **85**, 2172 (1963).

[7] Brady[5] has stated that acrylonitrile failed to produce a cycloadduct with diphenylketene.

[8] For an excellent review of vinylboron chemistry, see D. S. Matteson, *Organometal. Chem. Rev.*, **1**, 1 (1966).

[9] W. G. Woods, I. S. Bengelsdorf, and D. L. Hunter, *J. Org. Chem.*, **31**, 2766 (1966).

[10] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw Hill Book Co., Inc., New York, N. Y., 1959, p 132.

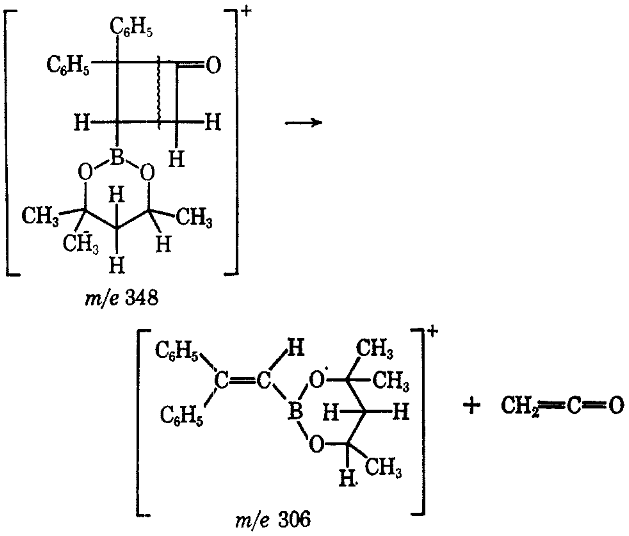


(1)

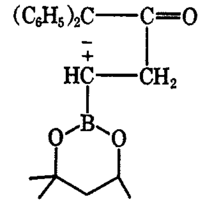
1

viously reported for cyclobutanones[11,12] Unfortunately, the X portion (c) was masked under the methyl groups of the dioxaborinane ring and only the sum of J_{ab} and J_{bc} could be determined.[13]

The remaining spectrum consisted of the aromatic protons [d, τ 2.70 (multiplet)], the tertiary dioxaborinane ring proton [e, τ 6.1 (multiplet)], the methylene group [g, which is the AB part of an ABX system (half of which is masked by the single methyl ring group) at τ 8.55], the single methyl group as a doublet [f, τ 8.93 (J_{ef} = 5.0 cps)], and the geminal methyls of the dioxaborinane ring [h, τ 9.06 (singlet)]. The mass spectrum at 70 eV provided added confirmation for the structure of **1** with peaks at *m/e* 348 (M^+ = molecular ion) and *m/e* 306 ($M^+ - CH_2=C=O$) in equal abundance.



The fact that the Woodward-Hoffmann rules[14] do not allow a thermal 2 + 2 concerted cycloaddition suggests that a two-step process for this type of cycloaddition reaction is in operation. (See Note Added in Proof.)[15] Since electrophilic olefins have not been found to undergo a cycloaddition reaction to diphenylketene, then a stepwise 1,2 dipolar and not a diradical cycloaddition has strong implications. Electrophilic olefins could stabilize a diradical intermediate but none of the possible dipolar intermediates. However, as stated previously, vinylborono compounds are able to stabilize dipolar intermediates such as I, by an electron-donating inductive effect, and hence their ability to form cycloadducts with diphenylketene.[16]



I

Experimental Section

2-(2′,2′-Diphenylcyclobut-3′-on-1′-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (1).—In a glass ampoule was placed 5.0 g (0.0256 mol) of diphenylketene and 3.96 g (0.0256 mol) of VTDB. The ampoule was heated in a bath at 110° for 360 hr. Distillation gave two fractions [I, bp 168–174° (0.30 mm), 0.6 g; and II, bp 174–177° (0.34 mm), 1.7 g], or a total of 2.3 g (26%) of product. The product solidified after a few weeks, and recrystallization from absolute ethanol produced white crystals, mp 89–91°.

Anal. Calcd for $C_{22}H_{25}O_3B$: C, 79.52; H, 7.58; B, 3.25. Found: C, 76.11; H, 7.26; B, 2.93 (analysis of C low on three determinations).

Registry No.—Diphenylketene, 525-06-4; 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane, 4627-10-5; **1**, 18741-96-3.

Acknowledgment.—The author would like to thank Mr. J. G. Whiten and Dr. W. G. Woods for a generous sample of VTDB.

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[11] K. Servis and J. D. Roberts, *J. Phys. Chem.*, **67**, 2885 (1963).

[12] H. O. House, S. G. Boots, and V. K. Jones, *J. Org. Chem.*, **30**, 2519 (1965).

[13] I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967). The negative coupling for J_{ab} is inferred from previous investigations on the sign of the couplings on cyclobutanone systems (ref 11 and 12).

[14] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 395 2046 (1965).

(15) NOTE ADDED IN PROOF.—After this Note was accepted for publication, Huisgen and coworkers published a study on the stereochemistry of the cycloaddition of diphenylketene to various olefins of known stereochemical configuration. Their results indicate a stereospecific cycloaddition reaction, and thus a modification of the Woodward-Hoffmann rules is in order. This modification brings in the fact that ketenes can be regarded as vinylium ylides. Thus stabilization of the transition state by a low lying π* antibonding orbital or the carbonyl group interacting with filled bonding orbitals of the olefin allows the ketene-olefin cycloaddition to be a thermally concerted process. However, this stabilization is greatly diminished when an electron-withdrawing group is placed on the olefin. See R. Huisgen, *et al*, *Tetrahedron Lett.*, 4485, 4491, 4497 (1968).

(16) D. S. Matteson and J. D. Liedtke, *Chem. Ind.* (London), 1241 (1963). These authors observed a similar stabilization of an α carbocation by the dibutoxyboryl group in the addition of HBr to dibutyl *trans*-but-2-eneboronate.

α,β-Unsaturated Sulfones *via* Phosphonate Carbanions

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Several routes[1–5] are available for the preparation of unsaturated sulfones from the corresponding β-hy-

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[1] D. L. Schoene, U. S. Patent 2,474,808 (1949), to U. S. Rubber Co.

[2] G. Kranzlein, J. Heyna, and W. Schumacher, German Patent 842,198 (1952), to Farbwerke Hoechst.