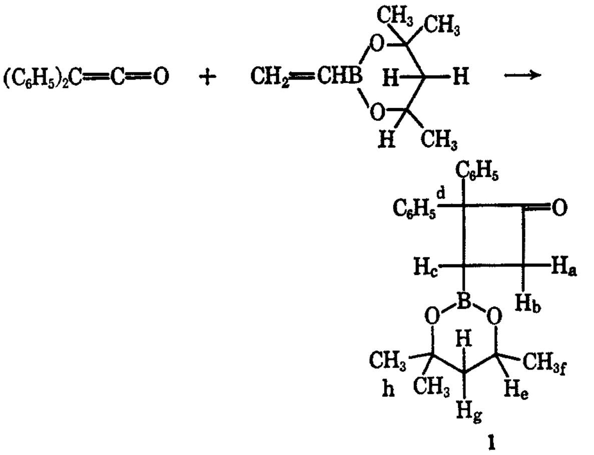
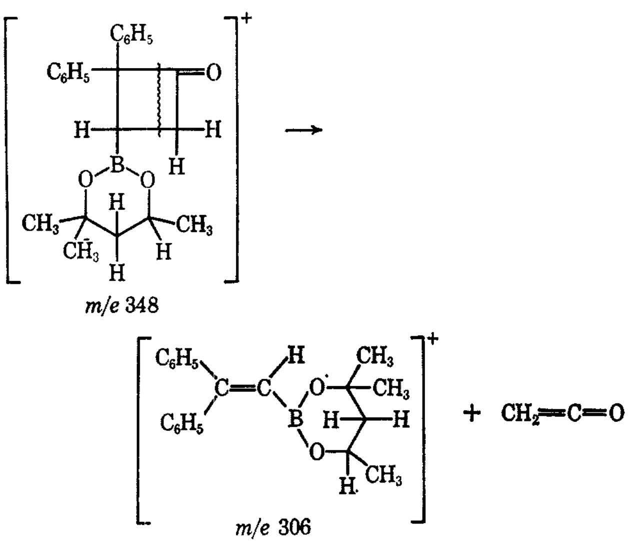


(1)

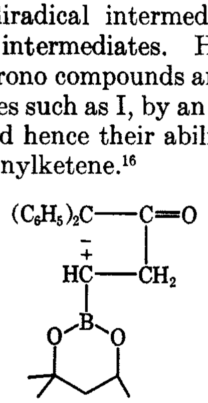
1

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.

---

(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

IVAN C. POPOFF, JAMES L. DEVER, AND GORDON R. LEADER

Pennsalt Chemicals Corporation,
King of Prussia, Pennsylvania 19406

Received July 25, 1968

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

---

(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.

TABLE I

$CH_3CH_2SO_2CH{=}CHR$

Product	R	Bp (mm) or mp, °C	Yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % S	Found, % C	Found, % H	Found, % N	Found, % S	Solvent Reactn	Solvent Recrystn
I	Ph	66–67	84	(Not analyzed)								*c*	*d*
II	3,4-$Cl_2C_6H_3$	117.5–118.5	91	45.28	3.77	*a*	12.07	45.73	3.95	*a*	12.41	*d*	*f*
III	4-$AcNHC_6H_4$	203–204	96	56.91	5.92	5.53	12.64	57.23	5.71	5.37	12.38	*d*	*f*
IV	2-Thienyl	46.5–48.5	93	47.52	4.95		31.68	47.76	5.13		31.69	*d*	*g*
V	2-Furyl	55.5–56.5	80	51.61	5.37		17.20	51.61	5.54		16.70	*c*	*d*
		115–117 (0.05)										*e*	
VI	2-(1-Me-pyrryl)	69.5–71	90	54.27	6.53	7.03	16.08	54.58	6.86	7.22	16.16		*h*
VII	2-Pyridyl	51–53	70	54.82	5.58	7.10	16.24	54.69	6.10		16.24	*d*	
		137–138 (0.05)											
VIII	3-Pyridyl	79–80	89	54.82	5.58	7.10	16.24	55.19	5.85	7.13	16.32	*e*	*h*
IX	4-Pyridyl	65.5–66	88	54.82	5.58	7.10	16.24	54.85	5.84	7.42	16.07	*e*	*h*
X	2-Quinolyl	84–85	77	63.17	5.26	5.66	12.96	63.55	5.55	5.77	13.02	*d*	*h*
XI	CCl_3	53.5–55	76	25.31	2.99	*b*	13.50	25.62	3.25	*b*	13.60	*d*	
		96–97 (0.1)											
XII	CH_2CH_2SMe	120–122 (0.05)	75	43.29	7.21		32.99	43.57	7.43		32.38	*d*	

[a] *Anal.* Calcd for Cl: 26.73. Found: 26.56. [b] *Anal.* Calcd for Cl: 44.93. Found: 44.49. [c] $MeOCH_2CH_2OMe$. [d] EtOEt. [e] $PhCH_3$. [f] MeCOMe. [g] EtOEt–petroleum ether (bp 30–60°). [h] EtOEt–PhH.

TABLE II

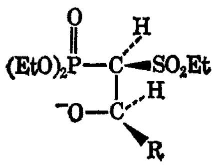
NMR SPECTRA

	$CH_3CH_2SO_2$ –CH_3 triplet, δ, ppm	$CH_3CH_2SO_2$ –CH_2– quartet, δ, ppm	–CH=CH– doublets, δ, ppm	J_{AB}, cps	Aromatic protons, δ, ppm	Solvent	Stereoisomer form
I	1.35	3.05	6.82, 7.54	15.5	7.44[d]	*h*	*trans*
II	1.39	3.14	6.91, 7.54	15.5	*e*	*i*	*trans*
III	1.27	3.16	7.18, 7.55	15.6	7.74	*j, k*	*trans*
IV	1.31	3.19	6.93, 7.82	15.2	*a*	*l*	*trans*
V	1.29	3.15	6.80, 7.39	15.3	*a*	*l*	*trans*
VI	1.31	3.19	6.92, 7.70	15.7	*e*	*l, m*	*trans*
VII	1.33	3.24	7.59, 7.59	*c*	*e, f*	*l*	*trans* ?
VIII	1.36	3.24	7.36, 7.72	15.5	*e*	*l*	*trans*
IX	1.36	3.28	7.57, 7.57	*c*	*g*	*l*	*trans* ?
X	1.37	3.27	7.75, 7.75	*c*	*a*	*l*	*trans* ?
XI	1.36	3.09	6.88, 7.22	14.5	None	*n*	*trans*
XII	1.30, 1.36	3.02, 3.14, *a*	*b*	*b*	None	*i*	*cis–trans*

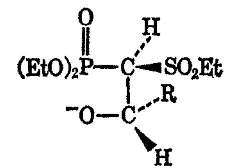
[a] Complex pattern. [b] Complex due to coupling to adjacent –CH_2–; prevents determination of *cis–trans* on the basis of number and splitting of lines; two singlets in the CH_3S– region at 2.03 and 2.12 ppm, and singlets at 2.62 and 2.67 ppm for –CH_2CH_2S–. [c] Singlet for vinyl protons because of chemical equivalence. [d] Narrow phenyl group band. [e] Superimposed on vinyl proton lines. [f] Weak, complex pattern. [g] Two doublets, superimposed on vonyl proton lines. [h] CCl_4–$CDCl_3$ 3:1. [i] $CDCl_3$. [j] DMSO–acetone 9:1. [k] CH_3-CO– singlet not observed because of interference by solvent. [l] Acetone. [m] CH_3N– singlet at 3.90 ppm. [n] CCl_4.

droxy sulfones. Another method makes use of a Knoevenagel-type condensation of aldehydes with alkylsulfonylacetic acids followed by decarboxylation.[6,7] A more convenient route utilizing the carbanion of diethyl ethylsulfonylmethylphosphonate[8] was investigated by us in a Wittig reaction,[9,10] and the results are summarized in Table I. It shows that the yields are quite high. For example, ethyl styryl sulfone (I) was prepared in 84% yield while the Knoevenagel-type reaction[7] resulted in 12% of I with unknown stereoisomerism. The majority of the products was purified by recrystallization. Four products were distilled and three of them solidified to low-melting crystals.

The very narrow melting point range of I–XI indicated that they represent one of the two stereoisomers rather than a mixture of both. This was confirmed by an nmr study which is summarized in Table II. It appears reasonable that the intermediate *threo* form which yields the *trans* isomer is preferred for I–XI, because of the greater steric hindrance in the *erythro* form. The R groups (see Table I) are bulkier for structure I–XI than for liquid XII which was found to be a mixture of both isomers. An additional explanation for the *trans* configuration of I–X can be seen in the stabilization of the incipient vinyl double bond due to its conjugation with R and $EtSO_2^-$. This conjugation is favored by the *threo* form for reasons of possible coplanarity of R and $EtSO_2^-$ with the new C=C.



erythro



threo

---

(3) E. F. Landau, U. S. Patent 2,554,576 (1951), to Celanese Corp.

(4) A. H. Ford-Moore, *J. Chem. Soc.*, 2433 (1949).

(5) W. Schumacher, PB 69,883 (1943), I. G. Farbenindustrie Hoechst.

(6) M. Balasubramanian, V. Baliah, and T. Rangarajon, *J. Chem. Soc.*, 3296 (1955).

(7) E. A. Fahnel and P. R. Resnick, *J. Org. Chem.*, **20**, 996 (1955).

(8) B. A. Arbuzov and N. P. Bogonostseva, *Zh. Obshch. Khim.*, **27**, 2360 (1957).

(9) S. Trippet, *Quart. Rev.* (London), **17**, 406 (1963).

(10) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, pp 132–212.

Considering the *trans* form of I–XI, and in support of what appears to be a stereospecificity of the reaction under the conditions applied by us, it is very likely that the *trans* isomer predominates in the 35:65 mixture found for XII.

Experimental Section

Starting Materials.—A 53.5% NaH suspension in mineral oil was used after the oil was removed by repeated washing with petroleum ether (bp 30–60°) and decanting. The aldehydes were freshly purified. The solvents were dry. The diethyl ethylsulfonylmethylphosphonate was prepared by the Arbuzov, *et al.*,[8] method and had bp 121–122° (0.04 mm) [lit.[8] bp 194° (4.5 mm)].

General Procedure.—To a suspension of 0.22 mol of NaH in 250–500 cc of solvent was added slowly 0.2 mol of diethyl ethylsulfonylmethylphosphonate over a period of *ca.* 20 min while stirring at 25–35°. The reaction mixture was stirred for additional 30 min at *ca.* 25° to allow completion of the H_2 evolution. A solution of 0.22 mol of the aldehyde in 30–50 cc of solvent was added dropwise to the reaction suspension over a period of 20–50 min while stirring at 25–35°. The suspension became thinner and a new, gummy solid [$NaOP(O)(OEt)_2$] started to precipitate. After an additional 50–60 min stirring at 20–35° the reaction was complete. The liquid phase was separated by decantation or filtration. In the cases where the product was soluble in the reaction solvent (products I, V, VI, VII, IX, XI, and XII) the solution was washed with water, dried and worked up to obtain the product. The products II and III were recovered by filtration of the reaction mixture and by washing the filter cake with water. In the remaining three cases, the products (*i.e.*, IV, VIII, and X) were partially soluble in the solvent and both the filter cake and the liquid phase were worked up for recovery of the product. Purification was achieved by distillation as indicated for each product in Table I.

Following are three examples for this general procedure, *i.e.*, the preparation of I, III, and XII.

Ethyl Styryl Sulfone (I).—To a stirred suspension of 5.3 g (0.22 mol) of NaH in 250 cc of $MeOCH_2CH_2OMe$ was added a solution of 49.9 g (0.2 mol) of diethyl ethylsulfonylmethylphosphonate in 50 cc of $MeOCH_2CH_2OMe$ over a period of 15 min at 25–30°. After an additional stirring for 20 min at 20–25°, the solution of 23.3 g (0.22 mol) of freshly distilled PhCHO in 30 cc of $MeOCH_2CH_2OMe$ was added in 25 min at 25–34° using cooling with ice-water when required. The reaction mixture was stirred for additional 25 min at room temperature and the liquid phase was separated by decantation from the gummy solid. The solution was evaporated to dryness *in vacuo* to obtain 38.3 g (98%) of a solid residue, mp 62–64°. It was recrystallized from EtOEt to recover 33 g (84%) of the *trans* isomer (see Table II), mp 66–67° (lit.[7] mp 66–67°).

4-Acetamidostyryl Ethyl Sulfone (III).—To the stirred suspension of the sodium salt of diethyl ethylsulfonylmethylphosphonate in 500 cc of EtOEt, prepared (as described above for I) from 6.2 g (0.256 mol) of NaH and 61.5 g (0.25 mol) of diethyl ethylsulfonylmethylphosphonate, was added 40.8 g (0.25 mol) of *p*-acetamidobenzaldehyde in 15 min while refluxing. After an additional refluxing for 1 hr the reaction mixture was filtered; the filter cake was triturated with 2 × 500 cc of H_2O and recrystallized from acetone to obtain 60.5 g (96%) of the *trans* isomer (see Table II), mp 203–204°.

Ethyl 1-(4-Methylthio)butenyl Sulfone (XII).—To the stirred suspension of the sodium salt of diethyl ethylsulfonylmethylphosphonate in 360 cc of EtOEt, prepared from 6.0 g (0.25 mol) of NaH and 57.6 g (0.24 mol) of diethyl ethylsulfonylmethylphosphonate, was added the solution of 25.0 g (0.24 mol) of 3-methylmercaptopropionaldehyde in 30 cc of EtOEt in 35 min at 25–35° using cooling by ice-water as required. After an additional 15 min stirring at room temperature the liquid was decanted from the gummy solid, washed with water, dried, and fractionated to obtain 34.7 g (75%) of the product, bp 120–122° (0.05 mm), n^{25}_{D} 1.5221. Its nmr spectrum established it as a 35:65 mixture of the two stereoisomers but did not prove which isomer is predominant (see Table II).

Nmr Studies.—The nmr spectra were recorded with a Varian DP-60 spectrometer with TMS as internal standard. The compounds were studied as 20% solutions in $CDCl_3$, CCl_4, acetone, DMSO or mixtures of these, and spectra were calibrated by the side-band method. The vinyl protons gave in most cases two doublets (AB system), or singlets in cases where their chemical shifts were identical. The doublet centers reported are the observed values rather than the corrected chemical shifts.

The coupling constant J_{AB} of 14.5–15.7[11a] cycles, the doublets for –CH═CH–, the single triplet for $-CH_3$, and the single quartet[11b] for $-CH_2-$ of $EtSO_2-$ of I–VI, VIII, and XI unequivocally prove that there is only the *trans* isomer present in these products. In the case of VII, IX, and X we also have one isomer but can not ascertain that it is *trans*. The two triplets for CH_3 in $EtSO_2-$, the two singlets for CH_3 in CH_3S-, and the two singlets for $-CH_2CH_2S-$ are criteria[11b] for the 35:65 mixture of the two isomers of XII.

Registry No.—I (*trans*), 18723-83-6; II (*trans*), 18723-84-7; III (*trans*), 18723-85-8; IV (*trans*), 18723-86-9; V (*trans*), 18723-87-0; VI (*trans*), 18723-88-1; VII, 18723-89-2; VIII (*trans*), 18723-90-5; IX, 18723-91-6; X, 18723-92-7; XI (*trans*), 18723-93-8; XII (*cis*), 18723-94-9; XII (*trans*), 18723-95-0.

[11] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Pergamon Press, New York, N. Y., 1966: (a) p 714; (b) p 739.

The Preparation and Electronic Spectra of *trans*-1,2-Vinylenebis(di-*n*-butylphosphine) and Its Monoxide

Michael A. Weiner and George Pasternack

Department of Chemistry, The City College of The City University of New York, New York, New York 10031

Received August 26, 1968

In a previous report from this laboratory,[1] the single peak above 220 mμ in the ultraviolet spectra of vinylphosphines was assigned to an electron-transfer type of transition, in which an electron is removed from the nonbonded orbital on phosphorus and transferred to the empty π* orbital of the vinyl group. Thus the excited state contains a negatively charged vinyl group. In the present study, *trans*-1,2-vinylenebis(di-*n*-butylphosphine) (1) has been prepared for the first time and its ultraviolet spectrum obtained. It is observed that the single peak above 200 mμ is significantly red shifted from the peak found in the spectrum of di-*n*-butylvinylphosphine (see Table I). This lowering of the transi-

Table I

Ultraviolet Spectroscopic Data

No.	Compound[a]	Solvent[b]	λ_{max},[c] mμ ($\epsilon_{max} \times 10^{-3}$)
1	$(n\text{-}C_4H_9)_2PCH{=}CHP(n\text{-}C_4H_9)_2$	I	263 (7.52)
	$(n\text{-}C_4H_9)_2PCH{=}CHP(n\text{-}C_4H_9)_2$	M	263 (6.60)
2	$(n\text{-}C_4H_9)_2PCH{=}CHP(O)(n\text{-}C_4H_9)_2$	H	266 (6.14)
	$(n\text{-}C_4H_9)_2PCH{=}CHP(O)(n\text{-}C_4H_9)_2$	M	273 (5.15)
3	$(n\text{-}C_4H_9)_2P(O)CH{=}CHP(O)(n\text{-}C_4H_9)_2$	M	*Ca.* 200[d]
4	$(n\text{-}C_4H_9)_2P(C_2H_3)$[e]	I	246 (2.60)
	$(n\text{-}C_4H_9)_2P(C_2H_3)$[e]	M	245 (2.63)

[a] All vinylene compounds have the *trans* configuration. [b] Isooctane (I), methanol (M), hexane (H). [c] Due to the broadness of the peak near the maximum, λ_{max} is reported only to the nearest millimicron. [d] Region of inflection. [e] See ref 1.

---

[1] M. A. Weiner and G. Pasternack, *J. Org. Chem.*, **32**, 3707 (1967).